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# Ion Exchange Derivatives of Cellulose.

Ronald William Rousseau

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The Louisiana State University and Agricultural and  
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ION EXCHANGE DERIVATIVES OF CELLULOSE

A Dissertation

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Louisiana State University and  
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in partial fulfillment of the  
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in

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by

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# TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vii
ABSTRACT	ix
CHAPTER I - INTRODUCTION	1
A. General	1
B. Cellulose and Cellulose Derivatives	4
C. Isocyanate Chemistry	25
D. Ion Exchange	35
References	48
CHAPTER II - EXPERIMENTAL APPARATUS AND PROCEDURES	53
A. Preparation of Reactants	53
B. Preparation of Cellulose Derivatives	56
C. Analytical Procedures	70
D. Evaluation of Properties of Cellulose Derivatives	78
E. Evaluation of the Possible Applications of Cellulose Derivatives	82
References	88
CHAPTER III - DISCUSSION OF RESULTS	89
A. General	89
B. Formation of Cellulose <i>p</i> -Toluenesulfonyl Carbamate	91
C. Characterization of Cellulose Derivatives	100
D. Application Studies on Cellulose <i>p</i> -Toluenesulfonyl Carbamate	123
E. Other Work on Cellulose Derivatives	139
References	143

	PAGE
CHAPTER IV - CONCLUSIONS AND RECOMMENDATIONS	144
A. Conclusions	144
B. Recommendations	146
APPENDIX A - TYPICAL EXPERIMENTAL DATA ON THE REACTION OF <u>p</u> -TOLUENESULFONYL ISOCYANATE WITH CELLULOSE	148
APPENDIX B - TYPICAL DATA ON ION EXCHANGE EVALUATION OF SULFONYL CARBAMATES	155
APPENDIX C - TYPICAL WORK ON NON-CARBAMATE CELLULOSE DERIVATIVES	158
VITA	161

## LIST OF TABLES

TABLE NUMBER		PAGE
CHAPTER I		
I-1	CELLULOSE DERIVATIVES - PROPERTIES AND USES	5
I-2	SOLUBILITY CHARACTERISTICS OF ETHYL CELLULOSE	6
I-3	CRYSTALLINITY MEASUREMENTS OF CELLULOSE	9
I-4	CELLULOSE CONTENT VS SOURCE	12
I-5	SWELLING AGENTS FOR CELLULOSE	15
I-6	CATALYSTS FOR ISOCYANATE REACTIONS	31
I-7	CATIONIC ION EXCHANGE CELLULOSES	44
I-8	ANIONIC ION EXCHANGE CELLULOSES	44
I-9	CAPACITIES OF CATION EXCHANGE MATERIALS	47
I-10	CAPACITIES OF ANION EXCHANGE MATERIALS	47
CHAPTER II		
II-1	TYPICAL FEED CHARGE TO ONE GALLON GLASS REACTOR USED IN MAKING SODIUM CARBOXYMETHYL CELLULOSE	60
II-2	TYPICAL REACTION CONDITIONS IN FORMING SODIUM CARBOXY METHYL CELLULOSE	60
II-3	TYPICAL FEED CHARGE FOR FORMATION OF PHENYL CARBAMATE DERIVATIVE OF CELLULOSE	63
II-4	TYPICAL REACTION CONDITIONS FOR FORMATION OF PHENYL CARBAMATE DERIVATIVE OF CELLULOSE	63
II-5	TYPICAL FEED CHARGE FOR FORMATION OF <u>p</u> -TOLUENE- SULFONYL CARBAMATE DERIVATIVE OF CELLULOSE	66
CHAPTER III		
III-1	CELLULOSE PHENYL CARBAMATE SPECTRA	103

TABLE NUMBER		PAGE
III-2	CELLULOSE <u>p</u> -TOLUENESULFONYL CARBAMATE SPECTRA	103
III-3	ALKALI SOLUBILITY OF CELLULOSE <u>p</u> -TOLUENESULFONYL CARBAMATE	110
III-4	SOLVENTS FOR CELLULOSE <u>p</u> -TOLUENESULFONYL CARBAMATE	111
III-5	A COMPARISON OF ION EXCHANGE CAPACITIES FOR CATIONIC ION EXCHANGE DERIVATIVES OF CELLULOSE	126



## LIST OF FIGURES

FIGURE NUMBER		PAGE
CHAPTER I		
I-1a	HAWORTH FORM FOR CELLULOSE	8
I-1b	ACTUAL STRUCTURE OF CELLULOSE	8
I-2	MECHANISM FOR DISRUPTING HYDROGEN BONDING	16
I-3	THEORETICAL OVERALL DISTRIBUTION OF SUBSTITUENT GROUPS IN CELLULOSE	21
I-4	MECHANISM IN PHOSGENATION OF ARYL SULFONAMIDES TO SULFONYL ISOCYANATES	28
I-5	SOME GENERAL REACTIONS OF SULFONYL ISOCYANATES	29
I-6	TITRATION CURVES OF CATION EXCHANGE RESINS	39
I-7	TITRATION CURVES OF ANION EXCHANGE RESINS	40
I-8	CLASSIFICATION OF ION EXCHANGE RESINS	41
CHAPTER II		
II-1	NITROGEN PADDING APPARATUS FOR BATCH REACTOR	64
II-2	DTA CELL OF DUPONT 900	80
II-3	SUBLIMATION TUBES FOR THERMAL DECOMPOSITION STUDIES	81
II-4	PHOTOGRAPH OF MICROFILM CASTER	85
II-5	CALIBRATION CURVE FOR MICROFILM FASTER	86
CHAPTER III		
III-1	DEGREE OF SUBSTITUTION VS REACTION TEMPERATURE	95
III-2	RATE OF ADDITION OF <u>p</u> -TOLUENESULFONYL ISOCYANATE TO CELLULOSE	97
III-3	IR SPECTRA OF KBr PELLET OF COTTON LINTERS	101
III-4	IR SPECTRA OF KBr PELLET OF CELLULOSE PHENYL CARBAMATE	102

FIGURE NUMBER		PAGE
III-5	IR SPECTRA OF KBr PELLET OF CELLULOSE <i>p</i> -TOLUENE-SULFONYL CARBAMATE	105
III-6	IR SPECTRA OF CELLULOSE <i>p</i> -TOLUENESULFONYL CARBAMATE FILM	106
III-7	IR SPECTRA OF KBr PELLET OF MIXED CELLULOSE CARBAMATES	108
III-8	SPECTRA OF PYRIDINE SMEAR OF CELLULOSE <i>p</i> -TOLUENE-SULFONYL CARBAMATE	113
III-9	DTA THERMOGRAM OF PURE COTTON LINTERS	115
III-10	DTA THERMOGRAM OF CELLULOSE PHENYL CARBAMATE	116
III-11	DTA THERMOGRAM OF CELLULOSE <i>p</i> -TOLUENESULFONYL CARBAMATE	117
III-12	DTA THERMOGRAM OF O-CYCLOHEXYL-N- <i>p</i> -TOLUENESULFONYL CARBAMATE	121
III-13	DTA THERMOGRAM OF SODIUM SALT OF CELLULOSE <i>p</i> -TOLUENESULFONYL CARBAMATE	122
III-14	TITRATION CURVE OF CELLULOSE <i>p</i> -TOLUENESULFONYL CARBAMATE	124
III-15	THEORETICAL LIMITS ON ION EXCHANGE CAPACITIES	128
III-16	EFFECT OF CROSSLINKING ON ION EXCHANGE CAPACITY	129
III-17	PHOTOGRAPH OF COATED METAL STRIPS	137

## ABSTRACT

A new class of cellulose derivatives, known as sulfonyl carbamates, has been developed in this research. These derivatives are formed by reacting pure untreated cellulose with sulfonyl isocyanates and have been found to possess many interesting and useful properties. Research was begun on this project in hopes that a new ion exchange resin could be developed. Sulfonyl carbamates were indeed found to possess a weakly acid character.

The *p*-toluene compound was selected as the sulfonyl isocyanate to use in investigating the synthesis of this derivative because of its commercial availability. Various reaction media were investigated but pyridine was the only one found to be effective in permitting reaction of untreated cotton linters. This was in spite of the fact that an insoluble complex is formed between *p*-toluenesulfonyl isocyanate and pyridine at temperatures below 70°C. Pyridine is effective as a reaction medium because of its ability to dissolve the reacted portion of the cellulose polymer. Data on the degree of substitution onto cellulose vs. reaction time show there is no measurable difference in the rate of addition of *p*-toluenesulfonyl isocyanate to the primary and secondary hydroxyl groups, even though the attainment of complete substitution (D.S. 3) is extremely difficult.

Infrared spectra of sulfonyl carbamate derivatives have been examined and are compared with those of other carbamate derivatives.

The solubility properties of the carbamate derivatives were investigated with particular emphasis being placed on evaluating the effect of degree of substitution upon solubility in a variety of

solvents. In general these derivatives were found to be soluble in dilute caustic (2%) but decreasing in solubility as the caustic strength was increased. Polar aprotic solvents such as dimethyl formamide and dimethyl sulfoxide were also found to be solvents for this derivative.

Differential thermal analysis of sulfonyl carbamates shows that their degradation occurs between 250 and 265°C. Controlled degradation along with isolation of decomposition products has led to the postulation of a six-centered reaction mechanism for the degradation process.

Studies on the ion exchange characteristics of sulfonyl carbamates have indicated the derivative to be weakly acidic with approximately the same strength as acetic acid. Ion exchange capacities were found to be significantly higher (avg.  $\sim 2.9$ ) than previously reported cellulosic ion exchangers. Crosslinking was needed to insolubilize the polymer and to control its swelling. Methylene bis-(p-phenyl isocyanate), chlorosulfonyl isocyanate, and p-isocyanatobenzenesulfonyl isocyanate were effective in accomplishing these goals. The ion exchange capacity passes through a maximum value as the degree of crosslinking is increased from .05:1 to .20:1 moles crosslinking reagent: mole of cellulose.

The application of cellulose p-toluenesulfonyl carbamate as a film has been examined. The films were cast from a pyridine solution and had good optical clarity. Plasticizer effects were noted for n-butyl phthalate. Attempts at crosslinking the films were not completely successful but were promising.

Metal coating with the sulfonyl carbamates also looks as if it has possibilities. Protection of metals from acids, organics, and

atmospheric conditions were noted.

Other areas of application were also investigated for the sulfonyl carbamate derivatives. Several other processes not involving isocyanates, but still pertaining to ion exchange derivatives, were evaluated and are discussed in the dissertation.

## CHAPTER I

### INTRODUCTION

#### A. General

Because of its natural abundance, and often flagrant waste, a better utilization of cellulosic materials is a challenge to the scientific and engineering professions. There are many well known sources of cellulose, including cotton, wood, bagasse, rice straw, and most other members of the plant kingdom. While plants may differ in the amount of cellulose in their constitution, they all contain enough to be considered a source of supply for cellulose. The research to be discussed in this dissertation was performed on purified cotton linters. However, there is no reason that the data obtained and the processes developed could not be applied to any of the other basic cellulosic materials.

In going over the work described in this dissertation, or in covering any material on the chemical modification of cellulose, it will be helpful to think of cellulose, not as a biological material, but as an organic polymer. The author has found that in discussing this work there is usually a problem of semantics unless this clarification is made.

Cellulose derivatives were the first of the man made high polymers and opened up a field which has grown to enormous proportions. There can be little doubt about the importance of polymers, for all one has to do is try to count all the polymeric materials he handles

or comes in contact with during a single day. It is also worthwhile to note that several new polymeric products and processes have been developed in the Department of Chemical Engineering at Louisiana State University. The first large scale process for the production of single cell proteins using waste cellulose was developed at these laboratories (1). In addition, techniques have been developed utilizing acrylic and cellulosic polymers in soil stabilization (2,3) and a process has also been developed utilizing the thermal decomposition products of cellulose as activated carbon and other useful organic reagents (4).

This list of accomplishments for a single laboratory in a relatively short period of time should point out the need for further research in this area. Hopefully, it should also indicate the utility of research on polymer systems as well as the broad range of studies which can be carried out in this field.

The work discussed in the body of this dissertation is aimed at producing new ion exchange materials using cellulose as a substrate for the attachment of ionogenic groups. Since, during the development of this process, it was found that such a derivative could be formed by reacting isocyanates with cellulose, the introductory chapter includes basic material on cellulose, cellulose derivatives, isocyanates, and ion exchange. Other possible applications were not investigated in as much detail as ion exchange and therefore are not covered in the introductory chapter but rather in the discussion of results.

In addition to the work done on the derivatives formed by reacting sulfonyl isocyanates and cellulose, other new products were

also investigated in lesser detail. They too will be covered in the discussion of experimental technique and the discussion of results. In any work of this sort there are always several attempted processes which fail. Because negative results often contribute to the overall knowledge in any given field, a brief discussion of these processes is also included in the discussion of results.



## B. Cellulose and Cellulose Derivatives

Besides the obvious reason of natural abundance, cellulose possesses several important physical properties which make it a useful high polymer. It is useful as a chemical intermediate because it is possible to chemically treat cellulosic materials enhancing their physical and chemical properties. The products from such treatments usually retain most of the desirable properties of the cellulose polymer even though the derivatives may possess properties which are radically different from the initial cellulosic material. These new properties are a function of the kind and quantity of substituent groups placed on the cellulose molecule. In Table I-1 some of these derivatives and their end uses are given. The list is not intended to be complete, but rather to indicate some of the various areas in which cellulose derivatives are used. In Table I-2 the solubility properties of ethyl cellulose are used to show how the properties of a given derivative can change by simply changing the degree of substitution (number of substituent groups per mesomeric unit).

It is precisely this variance in properties and uses which makes it worthwhile to continue synthesizing and studying new derivatives. Research in this area has not been lacking and yet, because of the physical problems in working with high polymers, cellulose chemistry is not the exact science one might think it to be. In the discussion which follows some of the important features which make cellulose an interesting and useful polymer will be briefly examined. For a more detailed discussion the reader is referred to several excellent general references (5, 6, 7, 8, 9).

TABLE I-1  
CELLULOSE DERIVATIVES - PROPERTIES AND USES (5)

<u>Derivative</u>	<u>Substituent</u>	<u>D. S.</u>	<u>Uses</u>
Nitrocellulose	$-\text{NO}_3$	1.8-2.0	Plastics molding compound
		2.1-2.3	Lacquers and cements
		2.3-2.9	Gun cotton
Cellulose Acetate	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{CH}_3 \end{array}$	2.2-2.3	Plastics molding compound
		2.3-2.4	Fibers and lacquers
		2.5-2.6	Films and tapes
		2.8-2.9	Insulating foils
Carboxymethyl Cellulose	$\begin{array}{c} \text{O} \\    \\ -\text{CH}_2\text{C}-\text{OH} \end{array}$	0.5-0.6	Detergent additive
		0.5-0.8	Textile and paper sizer
		0.8-1.2	Thickening agent

TABLE I-2

## SOLUBILITY CHARACTERISTICS OF ETHYL CELLULOSE (5)

<u>D. S.</u>	<u>Solubility</u>
0	Insoluble
0.5-0.7	Alkali soluble
0.7-1.3	Water soluble
1.4-1.8	Alcohol soluble
1.8-2.2	Soluble in common solvents
2.7-2.9	Soluble in hydrocarbons
3.0	Insoluble

## Cellulose Structure

Cellulose is a straight chain polysaccharide consisting of anhydroglucose units connected by a  $\beta$ -linkage (i.e., the alternating structures are rotated  $180^\circ$ ) in the 1,4-positions. Haworth (10) proposed the structure shown in Figure I-1a for cellulose. Because of its simplicity, this form is usually used even today. Figure I-1b gives what has been shown to be the actual structure of the cellulose unit. In contrast to the Haworth form, it shows the spatial arrangements of the atoms of the glucose unit as well as the chair structure of the pyranose ring. The spatial arrangements of the hydroxyl groups are also more clearly shown in Figure I-1b. Because of these advantages it is often helpful to consult the more detailed form when studying various cellulose reactions.

As can be seen from the illustrations, the functionality of cellulose, and therefore its ability to form derived products is based on its alcohol nature. The figures also show that each unit in the cellulose molecule possesses one primary hydroxyl and two secondary hydroxyls. The secondary hydroxyls are vicinal and occur in equatorial positions.

The degree of polymerization of cellulose (i.e., the number of anhydroglucose units in a single chain) is usually in the 3000-5000 range but varies as to the source of the cellulosic substance as well as to the amount and type of purification required. Degradation can be caused by several types of treatment and these will be discussed later.

When a group of cellulose molecules come into close proximity (such as occurs in nature), intermolecular secondary bonding is

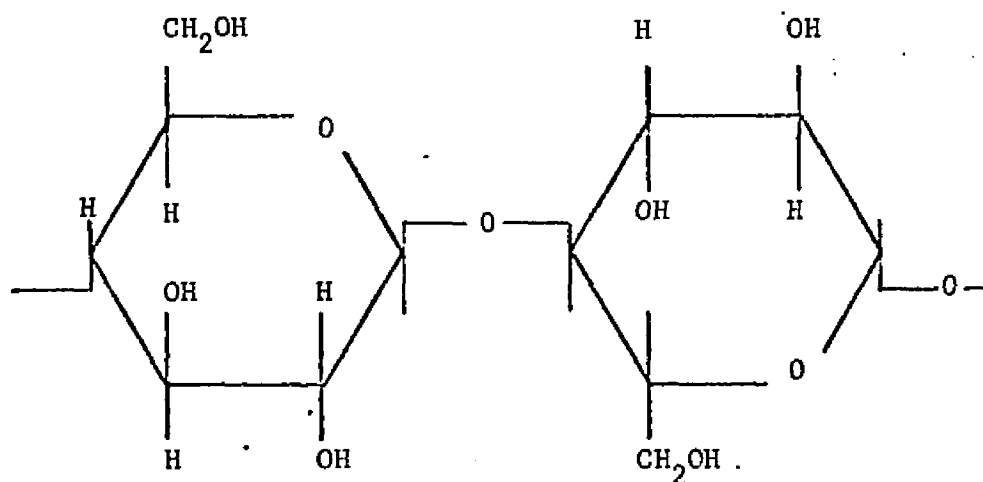


FIGURE I-1a: HAWORTH FORM FOR CELLULOSE (10).

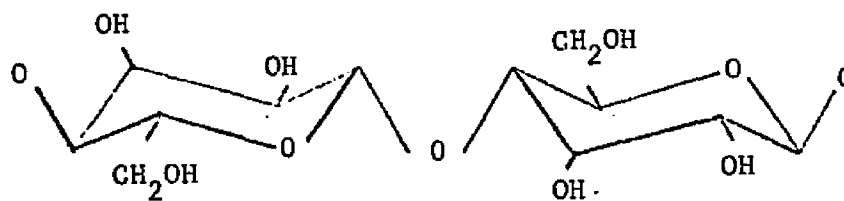


FIGURE I-1b: ACTUAL STRUCTURE OF CELLULOSE (11).

established. These bonds cause the molecules to agglomerate and form a larger structural species known as fibrils. These structures are between  $50 \text{ \AA}$  and  $100 \text{ \AA}$  in diameter and may be several thousand Angstroms in length. Fibrils possess regions of high crystallinity wherever regions of high molecular order is established as well as amorphous regions of low crystallinity. Table I-3 illustrates how cellulose crystallinity varies with its source and pretreatment. Crystallinity and how it effects cellulose reactivity will be discussed in a later section.

Table I-3	
CRYSTALLINITY MEASUREMENTS OF CELLULOSE (12)	
Cellulose	% Crystallinity
Wood pulp, hot alkali refined	70
Cotton linters, chemical grade	70
Cotton	69-71
Mercerized cotton	48
Mercerized wood pulp	48
Mercerized ramie	47
Regenerated cellulose (viscose rayon)	38-40

As the fibrils agglomerate, they form a fiber which is the largest structural classification for cellulose. Fibers can be as large as  $10,000 \text{ \AA}$  in diameter and can be of varying lengths. Natural cellulose is always in this form, never occurring in the free fibril or molecular forms. Nature has also provided a low molecular weight

polymer, known as lignin, to bind together cellulose fibers giving the cellulosic plants their structural strength. This polymer is usually removed before chemical modification of the cellulose is attempted.

### Cellulose Reactivity

By examining the structure of a cellulose molecule it is easy to see that cellulose reactions should parallel those of primary and secondary alcohols. Such a simplification would be misleading and sometimes incorrect for as already discussed, the natural state of cellulose is such that it does not exist in the free molecular form but rather in a larger polymolecular structure. Several factors contribute to this phenomena, but the most important are strong hydrogen bonding and the highly regular structure of the polymer molecules.

The strength of hydrogen bonding is most commonly and best illustrated by the high boiling point of a relatively low molecular weight substance like water, where the intermolecular attraction can be estimated by comparing its boiling point to that of other materials with approximately the same molecular weight. Hydrogen bonding in cellulose is aided by the regularity of the cellulose chains. The importance of the regular structure on the properties of cellulose is best illustrated by comparing its solubility with that of starch. Starch is made up of anhydroglucose units and should therefore have the same intermolecular attractive forces as cellulose. However, starch has branches which disrupt the molecular orientation required for strong hydrogen bonding and is therefore water soluble. On the other hand cellulose, which is linear and unbranched, is not solvated

by water.

Another example illustrating the effects of an ordered fibrous structure is the solubility properties of polyvinyl alcohol. As it is formed by the alcoholysis of polyvinyl acetate, polyvinyl alcohol is amorphous and water soluble. However, when a fiber is drawn from the amorphous system, the polymer molecules are oriented to maximize intermolecular attractive forces so that they cannot be solvated by water. It is because of the factors just described that cellulose is not dissolved and often not even swollen by reagents which might ordinarily solvate carbohydrates and alcohols.

Further important factors in cellulose chemistry are purity of the raw material, penetration of the cellulose structure by the reactant, the actual reaction mechanisms producing the desired derivative, uniformity of the final product, and possible cellulose degradation during reaction. Some of these factors are important in all chemical reactions, or only in reactions involving high polymers, and some are peculiar to cellulose reactions. At any rate, each of them will be discussed only in relation to cellulose chemistry.

#### Purification of Cellulose

Because native cellulosic materials vary in the amount of cellulose they contain, as shown in Table I-4, they also vary in the amount of purification required. The purest form of cellulose is that obtained from cotton linters which is also the main sources of chemical grade cotton cellulose. Cotton linters are the short fibers left on the cottonball after ginning has removed the larger cotton fibers. The non-cellulosic materials in cotton fibers are proteins, waxes, and pectin. These substances are removed by mechanical purification



followed by alkali extraction and a hypochlorite bleach. Corbett (13) gives a complete and detailed procedure for this process.

TABLE I-4	
CELLULOSE CONTENT VS SOURCE (12)	
<u>Source</u>	<u>% cellulose</u>
Wood	40-50
Cotton	88-96
Flax	80-90
Jute	65-75
Ramie	85

Cotton linters are relatively scarce when compared to the demand for chemical grade cellulose and therefore their use is limited to processes which require high purity and high molecular weight. Even in fields requiring these special properties, increasing amounts of wood cellulose is being used. Since wood is approximately 45% cellulose, considerably more purification is required for its processing. The major impurity to be removed from wood is lignin. Purification of wood cellulose involves chlorination of the pulp, alkaline extraction of impurities and hypochlorite bleaching. Hatch (14) and Green (15) discuss the details of this process.

Other cellulosic materials, such as bagasse, leaves, rice straw, etc., are somewhere between wood and cotton in cellulose content. Their purification can be carried out using modifications of the

techniques for wood and cotton.

A special problem in cellulose chemistry is that of moisture. Cellulose adsorbs water from the air so that cotton linters at equilibrium with the atmosphere typically contain from 5 to 8 percent moisture. When a treating process requires an anhydrous system, the procedure of drying cellulose become important. The simplest method of drying cellulose is by the use of a vacuum oven. Temperature in this type of oven may be kept in the 80-100°C range even though temperatures as high as 150°C may be used for a short time. Hot air drying can cause the capillaries which exist in the fibrillas structure of cellulose to collapse. This occurs because of the removal of water molecules from the capillaries and results in a loss of surface area of the polymer. With a loss of surface area, the number of sites available for attack by reacting species decreases. Green (16) uses solvent exchange to dry cellulose. Basically, the procedure calls for the cellulosic material to be soaked in several bathes of anhydrous methanol, allowing methanol to replace water in the capillaries, followed by bathes in the reaction medium, allowing it to replace methanol. This technique preserves the capillary structure of cellulose but is a tedious and expensive process, the returns of which may not be worth the extra effort.

Moisture can sometimes be removed by distilling the reaction mixture. This procedure calls for loading cellulose into the reactor along with the reaction medium. Water is then distilled from the system either azeotropically or by straight fractionation. To use this technique it is necessary that the solvent media boil somewhat higher than water or form an azeotrope with water. If the distillation

is carried out at too high a temperature degradation of cellulose begins so that it is usual practice to carry out the distillation under vacuum.

### Swelling of Cellulose Fibers

The complex macro structure of cellulose which was described earlier makes penetration (diffusion) of a reactant molecule to a reactive site a difficult task. Reaction mediums which swell cellulose or additives which accomplish this are almost mandatory in order to obtain any measurable degree of reaction. Some of the reagents which swell or dissolve cellulose are shown in Table I-5. All of these have the necessary functionality to break hydrogen bonding between cellulose molecules. A schematic representation of this process is shown in Figure I-2.

Of the swelling agents shown in Table I-5, sodium hydroxide solutions are the most often used. It is usually applied as a 5-50% solution, however, 12% is required before swelling becomes intracrystalline. Below this strength swelling occurs almost entirely within the crystallites. The desirability of using sodium hydroxide as a swelling agent can be attributed to its cheapness and ready availability. It is also important to note that excess sodium hydroxide, as well as its reaction side products, can easily be washed from cellulose and its derivatives after neutralization. In forming alkali cellulose (cellulose which has been treated with sodium hydroxide), oxidative degradation can be held at a minimum by keeping the mixture below the oxidation temperature and/or by having a nitrogen pad to eliminate the oxygen in the system. Caustic treatment disrupts the crystallinity of cellulose by forming a reactive complex with the hydroxyl groups

TABLE I-5

## SWELLING AGENTS FOR CELLULOSE (17)

9% sodium hydroxide + carbon disulfide

Calcium Thiocyanate

Cuprammonium hydroxide

Sodium hydroxide

Sulfuric acid

15% sodium hydroxide + carbon disulfide

Ruthenium red

Copper ethylenediamine

Phosphoric acid

85% formic acid + zinc chloride

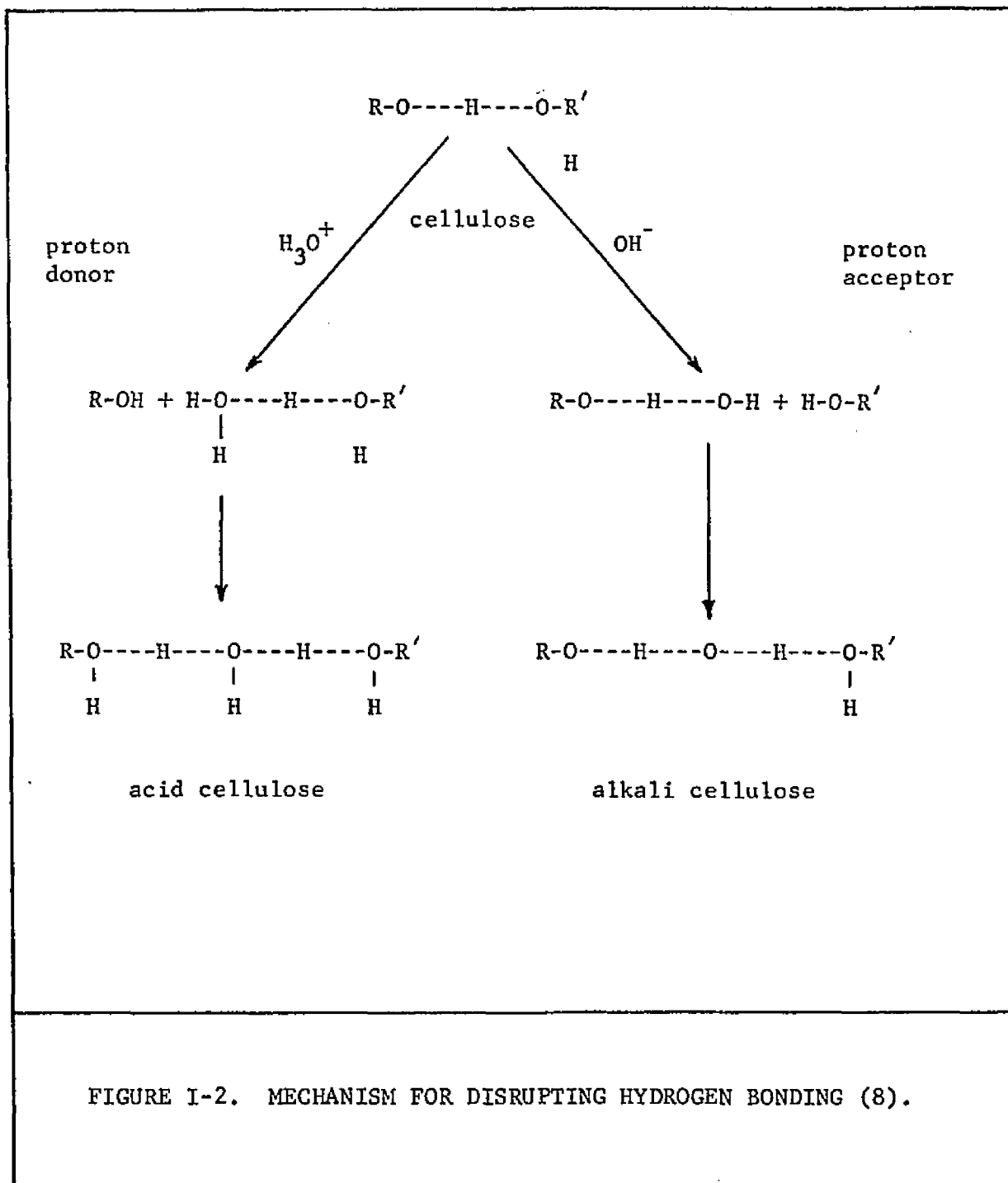
Trimethylbenzylammonium hydroxide

Iron tartrate complex

Methacrylate embedding

Sodium zincate

Cadoxen



on the anhydroglucose ring. Other alkali metal hydroxides may be used in place of sodium hydroxide with only slight variations in the degree of swelling.

Treatment of cellulose by sodium hydroxide and carbon disulfide is an important process, known as Xanthation, used in the manufacture of rayon and cellophane. Caustic disrupts cellulose crystallinity and  $\text{CS}_2$  reacts with cellulose to form cellulose Xanthate, a soluble derivative. The Xanthate group can then be hydrolyzed to regenerate cellulose.

Sometimes it is necessary that a particular process be anhydrous. When this is the case there are several possibilities for good swelling agents. Schnell (18) proposes the use of a  $\text{ZnCl}_2$  pyridine complex formed in excess pyridine to disrupt cellulose crystallinity. However, this may not be acceptable for some processes because of the difficulty in removing this complex from the polymer structure. Liquid ammonia has also been used to swell cellulose. Sodium cellulose can be formed quantitatively by adding pure sodium metal to an anhydrous slurry of cellulose in ammonia. Further reactions can then be carried out on the alkoxide form. The major problem found when working with a system such as this is that the ammonia has a strong tendency to remove water from the surrounding air causing loss of an anhydrous system.

Aprotic solvents may swell cellulose enough to permit reactions to occur. Dimethyl sulfoxide and dimethyl formamide have been used successfully for this purpose. Ellzey and Mack (19) used dimethyl formamide to swell cellulose in order to react it with phenyl isocyanate. Williams (20) utilizes a dimethyl sulfoxide-nitrogen dioxide

mixture to dissolve cellulose and permit further reaction. This process results in nitrite groups substituted on the cellulose chain so that the number of hydroxyl groups available for reaction has been diminished. In general, the use of aprotic solvents may be limited because their reactivity may cause them to react with the reagent being used to treat cellulose. Lewis bases such as pyridine have been used to swell cellulose by Ellzey and Mack (19). Lewis acids such as boron trifluoride etherate have also been used for this purpose.

Since the primary function of a swelling agent is to disrupt the regular crystalline structure of cellulose so that reactants can later penetrate to reactive sites, any other method of accomplishing this may be just as useful. Thus, if cellulose is reacted to a low degree of substitution, after the use of one of the swelling methods discussed, the derivative may be purified and used in further reactions. Klug (21) proposes reacting cellulose with ethylene oxide in the presence of caustic to produce a derivative (hydroxyethyl cellulose) with a degree of substitution of about .05-.1 for purposes of further reactions, whereas Callihan (22) uses a low D.S. carboxymethyl cellulose for this purpose. Cellulose acetate has been used for this purpose by several researchers (23, 24, 25). An advantage in using the acetate is that the acetate groups can subsequently be removed by hydrolysis with either acid or caustic. This method allows the use of relatively inert solvents (such as benzene, xylene, etc.) as a reaction medium for the desired reaction.

#### Chemical Reactions of Cellulose

Except for the physical phenomena of the transport of reactant through the cellulose, the reaction mechanisms of cellulose are

basically the same as those of smaller primary and secondary alcohols. Any good organic chemistry text discusses the reactions and mechanisms of these types of functional groups. It should be pointed out, however, that synthesis of a material by reaction of a low molecular weight alcohol does not prove the possibility of the corresponding cellulose reaction. This is particularly true for those reactions in which hydroxyl groups are replaced by such groups as  $-Cl$ ,  $-NH_2$ ,  $-CN$ ,  $-SR$ , and others. Usually the reaction steps for such processes would cause prohibitive degradation of the cellulose polymer.

Most of the reactions which can readily be performed on cellulose are ester and ether formation. The general references given at the beginning of this discussion cover specific reactions in greater detail than will be accorded them here.

Since the three hydroxyls are both primary and secondary, it might rightfully be assumed that there is a difference in reactivity among these groups. The primary hydroxyl (on the number 6 carbon) is generally considered to be more reactive. However, there is also a difference in the reactivity of the two secondary hydroxyls. Studies by Mahoney and Purvis (26) show first order rate constants for the tosylation of unsubstituted hydroxyls were in a ratio of 2.3 for the hydroxyl on the number two carbon, 0.07 for the hydroxyl on the number three carbon and 15 for the hydroxyl on the number six carbon. Further work by Purvis and Gardner (27) found that available hydroxyls reacted in the ratios of 2.16, 0.106, and 23.4 for the hydroxyls in the second, third, and sixth positions, respectively. While these values must obviously vary from reaction to reaction they give some idea as to the relative reactivity of the three hydroxyls.



### Uniformity of Substitution

One of the most important factors in the utilization of any polymer, or for that matter any material, is its uniformity. There would be little utility in a product whose physical properties varied only by removing a sample from a different portion of a storage bin. Since the physical properties of a cellulose derivative are largely determined by its degree of substitution, uniformity of physical properties for these materials implies uniformity of substitution. As has already been pointed out, this quality is often difficult to obtain for cellulose derivatives.

As in all other discussions involving cellulose reactions, the primary factor influencing product uniformity is polymer crystallinity. The amorphous regions of cellulose always are the first and often the only regions to react. The application of swelling agents helps in freeing the crystalline regions for reactions, but even if all regions of cellulose were equally accessible, Spurlin (28) has developed the statistics which shows that the theoretical over-all distribution of substituent groups is not perfect. A representation of the results of this work is shown in Figure I-3.

Regardless of these factors it is beneficial to strive for as uniform a degree of substitution as is possible. The methods in which reactions are carried out have a profound effect on product uniformity. There are five basic reaction systems which can be utilized in reacting high polymers. These methods will be discussed in terms of uniformity of the final product rather than on the basis of process economics.

From the standpoint of product uniformity then, the most

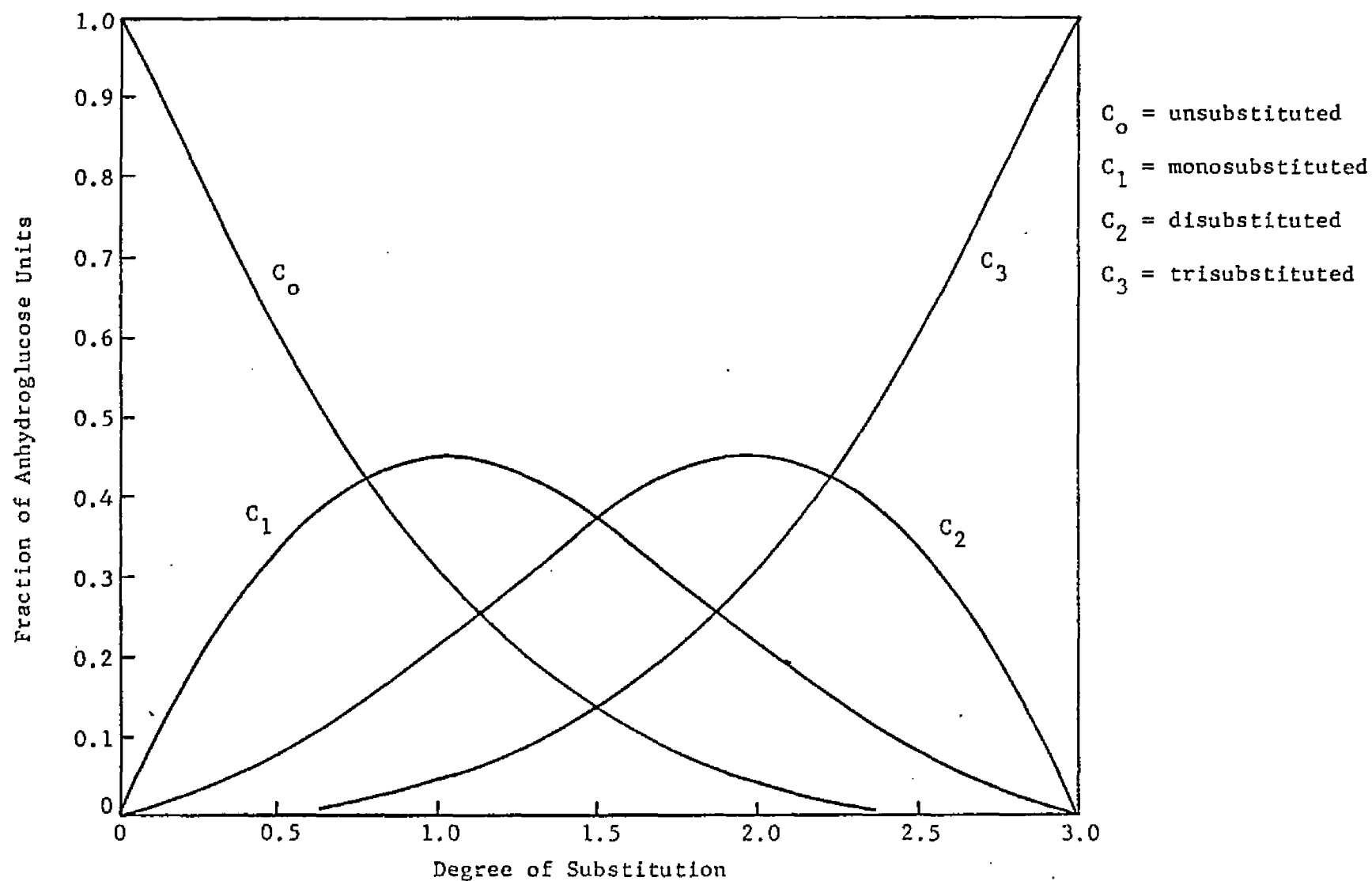


FIGURE I-3. THEORETICAL OVERALL DISTRIBUTION OF SUBSTITUENT GROUPS IN CELLULOSE FOR  $K_1:K_2:K_3 = 1:1:1$

desirable system would involve utilizing a solvent such that both the initial polymer and its final derivative would be in solution. This system would insure that all reactive sites on a polymer substrate would have an equal chance of reacting and thus the maximum possibility of uniform substitution. As already discussed the possibility of using this type of system for cellulose reactions is limited by the lack of good solvents for cellulose.

Next in desirability is that system which utilizes a reaction medium which, although it does not dissolve the initial polymer, dissolves the final derivative. Since a goodly number of cellulose derivatives are soluble in one reagent or another, the possibility of utilizing this type of system for cellulose reactions is quite good. Usually, however, rather than using enough solvent to give a good solution, only enough is used to form a paste (or "dope") with the derivative. The commercial preparation of cellulose acetate utilizes this type of system.

Using a reaction medium which is a solvent for the initial polymer but not for its derivative would be next in desirability. As the polymer reacts it falls out of solution. Precipitation of the polymer in this manner tends to "cage" in reactive sites making them inaccessible to reactant. Since there is a difficulty in finding solvents for cellulose this type of system is not extensively used. It can be used in reacting derivatives of cellulose and can also be important in crosslinking reactions. When a polymer in solution is treated with a crosslinking agent, it either precipitates, in which case further reaction is limited, or it sets up into a gel, in which case further reaction is not effected. Lenz (29) relates that the

free diffusion of reactant molecules in the gel is no different than in the viscous solution which preceeded crosslinking.

The fourth system is that which utilizes a reaction medium in which both the initial polymer and its derivative are insoluble. It is in this type of system that the amorphous region are reacted to a greater extent than the crystalline regions. Thus it is this type of system which requires the application of the swelling agents previously discussed. This system is used in a large number of the commercial preparations of cellulose derivatives.

The fifth method of reaction of a polymer involves no solvent carrier. Theoretically, this method would be the least efficient in producing a uniform product. However, because of the economic desirability of not having to use a solvent is gradually being accepted by commercial producers of cellulose derivatives.

#### Cellulose Degradation

The term degradation is used throughout this text to denote any process which decreases the molecular weight (or degree of polymerization) of a polymer molecule. The importance of molecular weight in controlling the physical properties of a polymer cannot be over emphasized. In forming cellulose derivatives one is usually trying to take advantage of the high molecular weight of natural cellulose; thus, those environments which lead to degradation are avoided when at all possible. There is little to be gained by using reaction conditions favorable for reacting cellulose hydroxyls if the molecular weight of the final product is so low as to render the derivative useless.

Since cellulosic polymers are generally more susceptible to

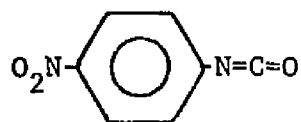
degradation than other types of polymers (e.g. the vinyl polymers) their processing is usually carried out under rather mild conditions. As discussed throughout the techniques of drying and reacting cellulose, heat can substantially degrade its molecular structure. McBurney (30) reviews the mechanisms of thermal degradation as well as degradation by light, oxidation and mechanical means. Because cellulose is extremely difficult to dissolve, those chemicals which do act as solvating agents usually exert the types of intermolecular forces which lead to chemical degradation. Acid solvents lead to hydrolytic degradation of the acetal linkage, for which the only retardant is the lowering of the solution temperature. In alkaline solvents, the degradation is oxidative, which may be minimized by oxygen exclusion and low temperatures. Nicoll, Cox and Conway (31) review alkali degradation of cellulose in detail.

Microbiological degradation of cellulose has been investigated by Dunlap (1) who utilizes degradation in a constructive manner by using cellulose as a food for microorganisms in the production of single cell proteins. Another degradation process has been developed by Williamson (4) using chemical and thermal degradation to produce useful organic reagents from waste celluloses.

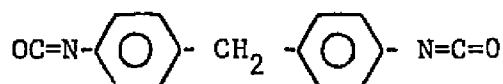
These are some of the phenomena which must be considered in any postulated process for production of a cellulose derivative. In the work that follows the importance of each of these factors will be illustrated, especially in explaining some of the observed phenomena in the reactions of isocyanates with cellulose.

### C. Isocyanate Chemistry

Isocyanates are those chemical compounds having the functional group  $-N=C=O$ . This group may be attached to either an aliphatic or an aromatic structure. Typical nomenclature for these substances is illustrated by para-nitrophenyl isocyanate (I).



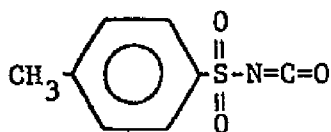
(I)



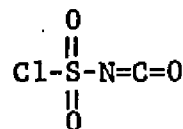
(II)

Dissocyanates are named in a similar manner although there may be some confusion as illustrated by methylene bis-(p-phenyl isocyanate) (II) which is also known as bis-(4-isocyanatophenyl) methane.

Besides these types of isocyanates, there exists a subclassification of these compounds known as sulfonyl isocyanates. The functional group of these compounds has been modified by placing a sulfonyl group between the isocyanate function and the substrated ( $-SO_2-N=C=O$ ). The presence of the sulfonyl group radically alters the chemical properties of those materials and thus it is necessary to consider them as a unique chemical species. Nomenclature of sulfonyl isocyanates is similar to that of regular isocyanates. Two good examples of the naming of these compounds are para-toluenesulfonyl isocyanate (III) and chlorosulfonyl isocyanate (IV).

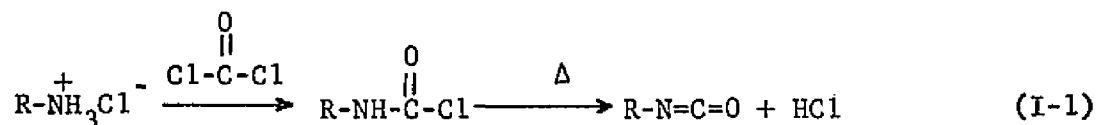


(III)

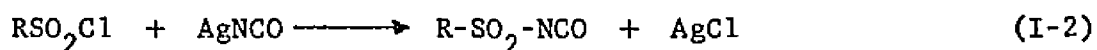


(IV)

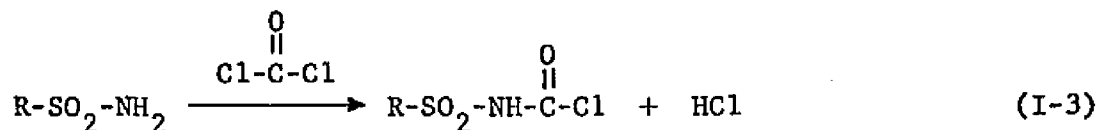
Isocyanates have been easily synthesized for a number of years by direct phosgenation of primary amine salts as shown by Equation (I-1).



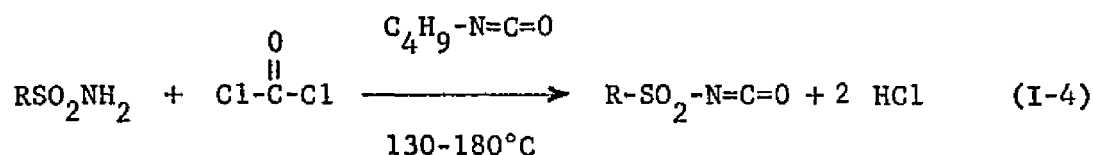
Even though this procedure has worked well for isocyanates, the lack of interest in sulfonyl isocyanates has been mainly due to the difficulty in their preparation. Classically, the synthesis of sulfonyl isocyanates required the reaction of sulfonyl chloride with silver cyanate in benzene as shown in Equation (I-2). It is not difficult to



imagine the problems associated with such a scheme; not only did the reaction have low yields but silver cyanate is an expensive chemical which could not be easily recovered or regenerated. When direct phosgenation of a sulfonamide was tried, as in Equation (I-3), the



result was the formation of the stable intermediate shown in Equation (I-3), rather than the sulfonyl isocyanate. Ulrich and Sayigh (32) subsequently developed a process allowing aryl sulfonamides to be phosgenated directly in the presence of catalytic amounts of an alkyl isocyanate as shown in Equation (I-4). The actual mechanism of this



reaction is shown in Figure I-4. Temperatures required for this reaction are between 130-180°C and yields are in the 85-90% range. It is also useful to note that there are no problems in separating the reaction products. Sulfonyl isocyanates have higher boiling points than the corresponding alkyl isocyanates or the other end products so that a separation of the products can be easily effected by distillation.

Isocyanates have been used extensively in the manufacture of urethane foams and more recently in the preparation of the spandex fibers. However, the aforementioned problems in synthesis of sulfonyl isocyanates has limited their adoption for such uses. Since more efficient methods of production have been developed some of the possibilities of using these materials as an intermediate should be investigated. In order to do this a knowledge of the chemistry of these compounds is necessary. A review article on the whole field of sulfonyl isocyanates has been written by Ulrich (33) and several less comprehensive reviews covering some of the specialized fields have also been written (34, 35, 36). A general summary of the major reactions discussed in these articles is given in Figure I-5.

In general, isocyanates react with alcohols as shown in Equation (I-5) to form compounds known as carbamates. The mechanism predicts



# Synthesis of Sulfonyl Isocyanates

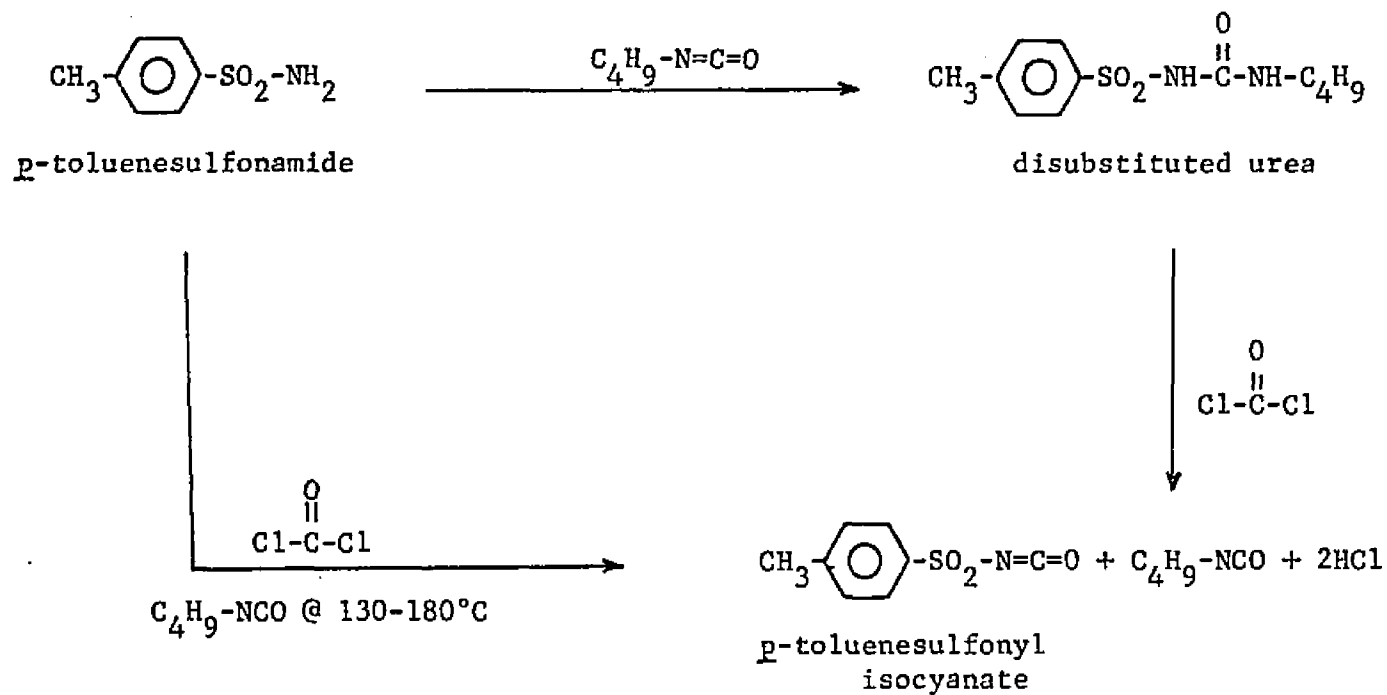


FIGURE I-4. MECHANISM IN PHOSGENATION OF ARYL SULFONAMIDES TO SULFONYL ISOCYANATES.

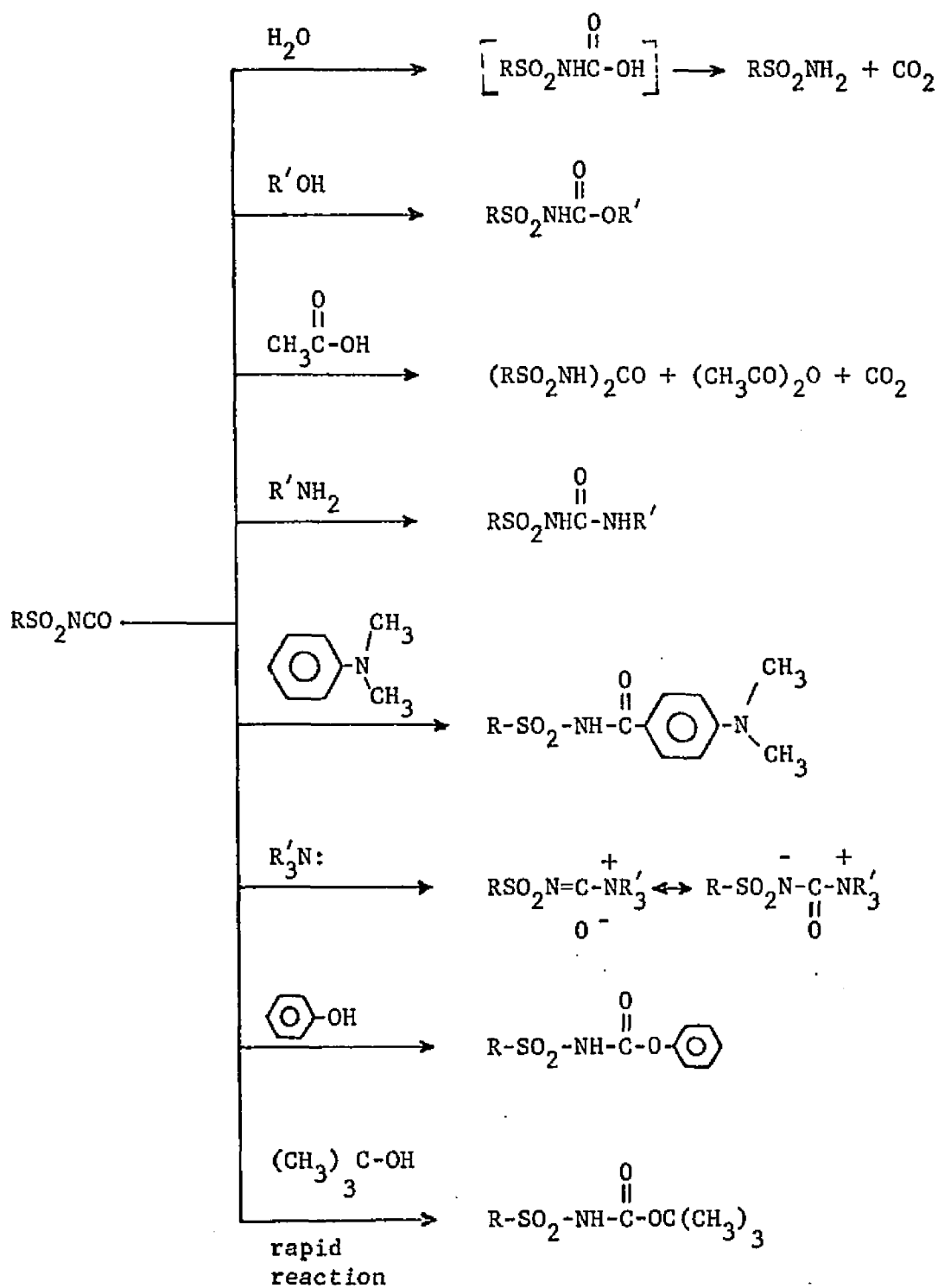
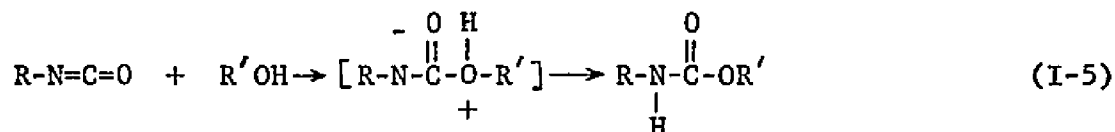
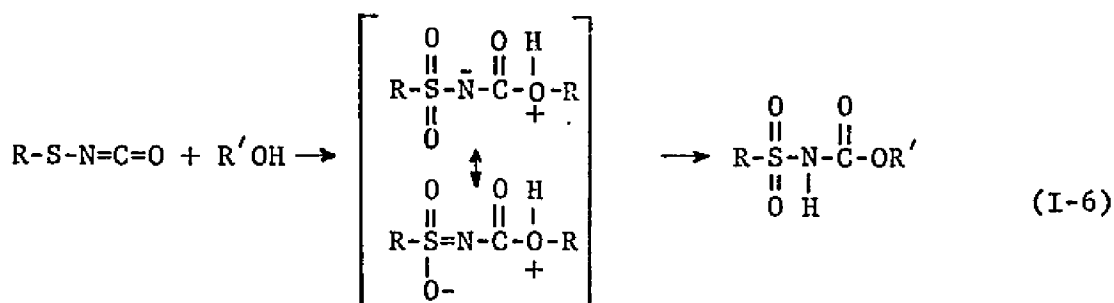


FIGURE I-5. SOME GENERAL REACTIONS OF SULFONYL ISOCYANATES.



the formation of a transitory intermediate shown in brackets. The transition state may be stabilized, and thus the rate of reaction enhanced, if the R- groups have electron withdrawing ability. Picturing the same mechanism for sulfonyl isocyanates, as in Equation (I-6), it would be expected that the electron withdrawing

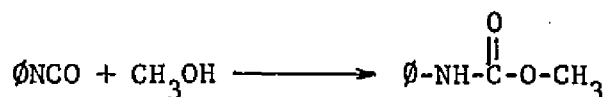


ability of the sulfonyl group would cause sulfonyl isocyanate to be much more reactive than isocyanates. This is demonstrated by the fact that isocyanates usually require catalysts to stabilize the transition state whereas there is no need for using catalysts when reacting sulfonyl isocyanates. The type of compounds which can be used to catalyze isocyanate reactions are listed in Table I-6 and a complete review of the principles involved is given by Saunders and Frisch (38).

Besides differing in reactivity sulfonyl isocyanates also differ from isocyanates in the types of substrate to which the respective functional groups can be attached. The sulfonyl isocyanate group may be attached to a halogen atom rather than be limited to alkyl and aryl groups as isocyanates are. For example, the preparation of chlorosulfonyl isocyanate has been established on a commercial scale.

TABLE I-6

CATALYSTS FOR ISOCYANATE REACTIONS AND  
RELATIVE ACTIVITY FOR THE REACTION



<u>Catalyst</u>	<u>Relative Rate (37)</u>
None	1
$(\text{CH}_3\text{CH}_2)_3\text{N}$	11
1,4 diazobicyclo octane (DABCO)	110
$\text{Co}^{++}$ [naphthenate]	23
$\text{Sn Cl}_4$	99
$(\text{C}_4\text{H}_9)_2 \text{Sn}^{++}$ [dilaurate]	37,000

The fluoro derivative has also been prepared but is not available commercially. The existence of these two types of functional groups on the same molecules makes them very reactive. Graf (39) has written a review discussing these compounds and some of their unique characteristics. He has also published a detailed laboratory synthesis technique for chlorosulfonyl isocyanate (40).

#### Carbamate Derivatives of Cellulose

Since cellulose exhibits alcoholic functionality it should react with isocyanates in much the same manner as lower molecular weight substances. As discussed previously in the section on cellulose chemistry, such reaction is limited by the physical structure of the polymeric cellulose molecules. In particular, the lack of easy accessibility of hydroxyl groups presents several problems. Many

investigators of this reaction corrected for this problem by using partially acetylated cellulose for the polymer substrate (23, 24, 25) while others used methyl cellulose (41). These derivatives were used rather than expose cellulose itself to the extreme conditions of high reaction temperature for long periods of time which would otherwise be required. Other approaches to this problem have been to regenerate cellulose by hydrolyzing cellulose acetate in anhydrous ammonia (42), pretreatment of cellulose with caustic followed by solvent exclusion (42), or treating cellulose with a  $\text{ZnCl}_2$ : pyridine complex (18). All of these procedures are designed to disrupt cellulose crystallinity and allow penetration of the desired reactant to the hydroxyl groups.

Ellzey and Mack (19) examined the effect of various solvents on the reaction of phenyl isocyanate and cellulose. Their work shows that unless a solvent can swell cellulose, there will be no reaction. Pyridine and N,N- dimethyl formamide were the only mediums tested which gave extensive reaction. No reaction occurred when using media which did not swell cellulose, e.g. toluene. It should be noted that those reagents which gave reaction also dissolved the substituted cellulose polymer, giving a viscous homogeneous mixture. Thus it may be that in addition to swelling cellulose a primary requirement for reaction of this type may be solution of the cellulose derivative.

Hearon and Lobsitz (25) discuss the reactivity of various aryl isocyanates with cellulose acetate. This work shows the effect of various substituent groups on the phenyl ring of phenyl isocyanate on the rates of their reactions with cellulose. The rates were found to be p-bromophenyl > o-chlorophenyl >  $\alpha$  naphthyl > phenyl > p-tolyl > o-tolyl. This corresponds to the theory of the more stabilizing the

substituent group to the transition state, the more rapid the reaction.

Various catalysts for isocyanate reactions with cellulose have been studied. Ellzy and Mack (19) used dibutyl tin diacetate as a catalyst while Voloshin, Kozmina, and Danilov (42, 43) have studied the catalytic effects of dibutyl tin dilaurate and tertiary amines. Transition metal catalysts produce faster rates than the amines. Among the amines the order of reaction enhancement has been found to be triethylamine  $\geq$  trihexylamine  $>$  tribenzylamine  $>$  pyridine. It might be noted that the stronger the basicity of the amine the greater the catalytic effect of these amines. However, steric factors are also important as illustrated by the fact no rate enhancement is caused by diethyl aniline, a stronger base than pyridine.

Hydrolytic stability of carbamate derivatives of cellulose acetate was studied by Hearon, Hiatt, and Fordyce (24). They found that acid hydrolysis occurred at the acetate linkages but did not occur at the carbamate linkages even at higher temperatures. While some hydrolysis of the carbamate linkages under strong alkali conditions were noted, it was slight and usually negligible. This led Breslow (44) to surmise that since these linkages were stable to acid hydrolysis they could be used to attach groups which would yield an acid soluble derivative. He accomplished this by reacting N,N-dimethyl-4-isocyanato aniline and other similar compounds with cellulose. Schnell and Rinke (45) used phenyl carbamate derivatives of cellulose and cellulose acetate to produce coatings which they claimed had reduced water absorption and improved electrical resistance.

Mack and Hobart (46) have studied the thermal behavior of cellulose carbamates and have found these materials to be fairly stable,

decomposing at about 225-250°C to the isocyanate and cellulose. They further showed that electron-withdrawing groups on the aromatic nucleus of phenyl isocyanate increased the thermal stability of the cellulose carbamate linkage and electron-donating groups decreased the thermal stability.

The reaction of cellulose with diisocyanates to produce a cross-linked carbamate structure has been tried by Mack and Hobart (46). They were not successful and their failure was attributed to reaction at the fiber surface. They surmise that reaction at the surface tightly crosslinks the polymer molecules and does not allow further penetration of reactant. Rousseau, Daly, and Callihan (47) used methylene bis (p-phenyl isocyanate) to crosslink cellulose derivatives which have been dissolved in the given reaction medium (44).

#### D. Ion Exchange

Ion exchange is probably one of the least familiar separation techniques. Partly because of this obscurity it is also one of the least used unit operations. Ion exchange remains relatively unknown even though Thompson (48) and Way (49) recognized its features as early as 1845. In 1905 Gans (50) developed the first commercial scale ion exchange operation in softening water and removing calcium ion from sugar syrup. Adams and Holmes (51) developed the first synthetic ion exchange resin in 1935 based on a phenolformaldehyde matrix. Since 1935 continuing research has provided numerous new areas of application for ion exchange materials; some of these will be discussed later. In general, however, this brief discussion of ion exchange will concern the more recent work in the field. For a detailed history of ion exchange the reader should consult books by Kunin (52) and Inczedy (53).

Kunin defines ion exchange as a reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. The solid being known as an ion exchange resin. Because there can be no substantial change in the structure of the solid during the transfer of ions, systems must be chosen which are insoluble in the liquid. For this reason most ion exchange resins are polymeric in nature and often have some degree of crosslinking.

Michalson (54) discusses several industrial applications of ion exchange and also gives details on the types of equipment as well as the methods of operation for both continuous and fixed bed systems. Also discussed are some of the economics involved in operating and



building large scale ion exchange processes.

Besides large scale processes, ion exchange has also been used in many analytical chemistry procedures. Chromatographic column separation techniques and the associated equipment are described in detail by Inczedy (53) as well as various micro separation techniques used in both qualitative and quantitative analysis. A new and unique method for separating stereoisomers by using assymetric ion exchangers has been proposed by Buss and Vermeulen (55). Sober and Peterson (56, 57) developed a procedure for fractionating proteins and other biological chemicals using cellulosic ion exchange. Their effort is a classic piece of work in the field of ion exchange.

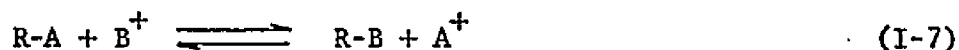
Regardless of which of the above applications an ion exchanger is being used in, most of these materials have several common characteristics. Not only should ion exchange resins be insoluble, but they should also have limited swelling characteristics. It is true that the greater the swelling the more available are sites for ion exchange, but passing a liquid through a bed of highly swollen polymeric solids would require too high a pressure drop and consequently limit the possible flow rates. Other important characteristics of ion exchangers are the stability of such materials to both attrition and to the chemical environment expected for these resins. The regeneration of ionogenic groups from the species formed during a process to that at the beginning of the process is also mandatory and is usually accomplished by exposure of the resin to a stream containing a high concentration of the initial ion present on the ionogenic group. A further requirement is that the ion exchange capacity, or the number of exchangeable ions per unit by weight, be reasonably high.

While the factor can vary in importance depending on the particular application, it must always be considered when developing a new ion exchange material and indeed there has been many efforts devoted to increasing capacities of existing resins.

Besides these common requirements, there are also three ways in which an ion exchange resin may be categorized. These are as follows:

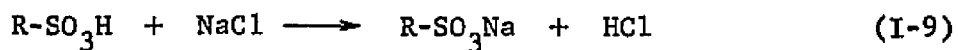
1. The type of ionogenic group possessed by the resin.
2. The base or substrate to which the ionogenic groups are attached.
3. The physical form of the resin

Ionogenic groups are those groups which give a resin its ion exchange capability. There are two fundamental groupings of ion exchangers depending on the acid-base characteristics of the ionogenic groups. If the group is acidic, and therefore exchanges cations as shown in Equation (I-7), it is known as a cationic ion exchange resin. On the other hand, if the group is basic its ion exchange mechanism is illustrated by Equation (I-8) and it is known as anionic ion exchange resin.



There are also further subclassifications according to the acidic or basic strength of the ionogenic groups. Strong acid ion exchange resins possess ionogenic groups which remain highly ionized in both the acid and salt forms. Because of this high degree of ionization, they show ion exchange capabilities over the full pH range and can therefore convert a neutral salt to the corresponding acid by the

mechanism shown in Equation (I-9) which uses a sulfonic acid resin



as an example. This property is known as salt splitting ability and is not possessed by weakly acidic ion exchange resins. Weak acid resins are those operable only in the pH range above 7. A further illustration of the difference between strong and weak acid resins is demonstrated in the titration curves shown in Figure I-6. A corresponding subdivision of basic ion exchange groups is made and typical titration curves for weakly and strongly basic resins are shown in Figure I-7. Figure I-8 gives a schematic breakdown of the various classifications of ion exchange resins as well as some of the uses of the subdivisions.

The type of base or substrate to which ionogenic groups are attached are important in two main respects. First, the substrate must be unaffected by both the chemical environment and the physical stress occurring in the ion exchange process. A substrate is not useful if it degrades or depolymerizes under operating conditions, nor is it useful if it is subject to physical degradation. Secondly, the nature of the substrate can effect the rate of transfer of ions. For example, a hydrophobic substrate, such as polystyrene, will decrease the rate of transfer of an ion solvated by water. This is usually minor however since the ionogenic groups themselves are usually hydrophilic enough to offset this effect.

The physical form of the resin is often set by the way in which it is polymerized but in some cases it can be adjusted for specific applications. Since many of the resins are formed in suspension, or

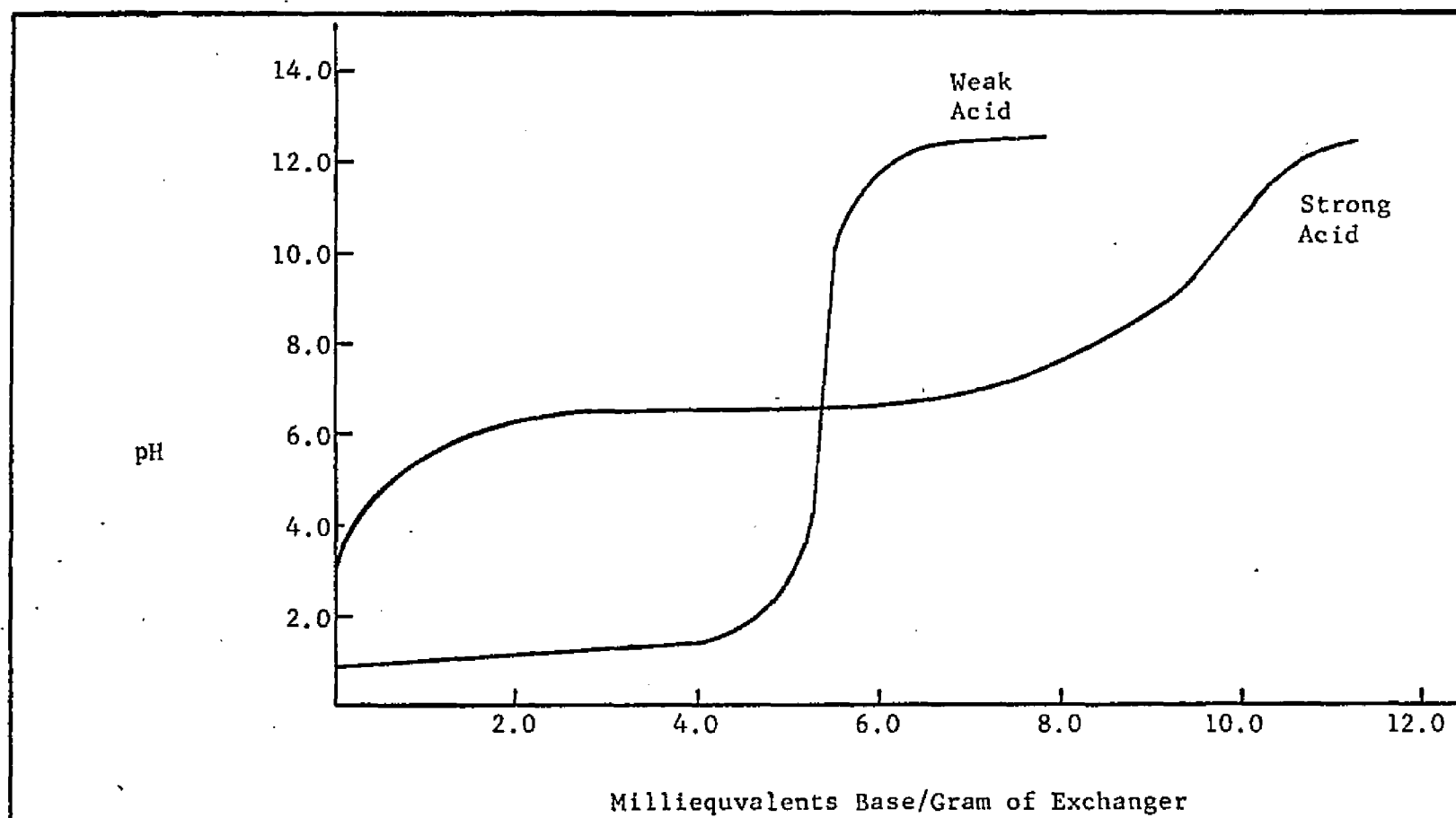


FIGURE I-6. TITRATION CURVES OF CATION EXCHANGE RESINS.

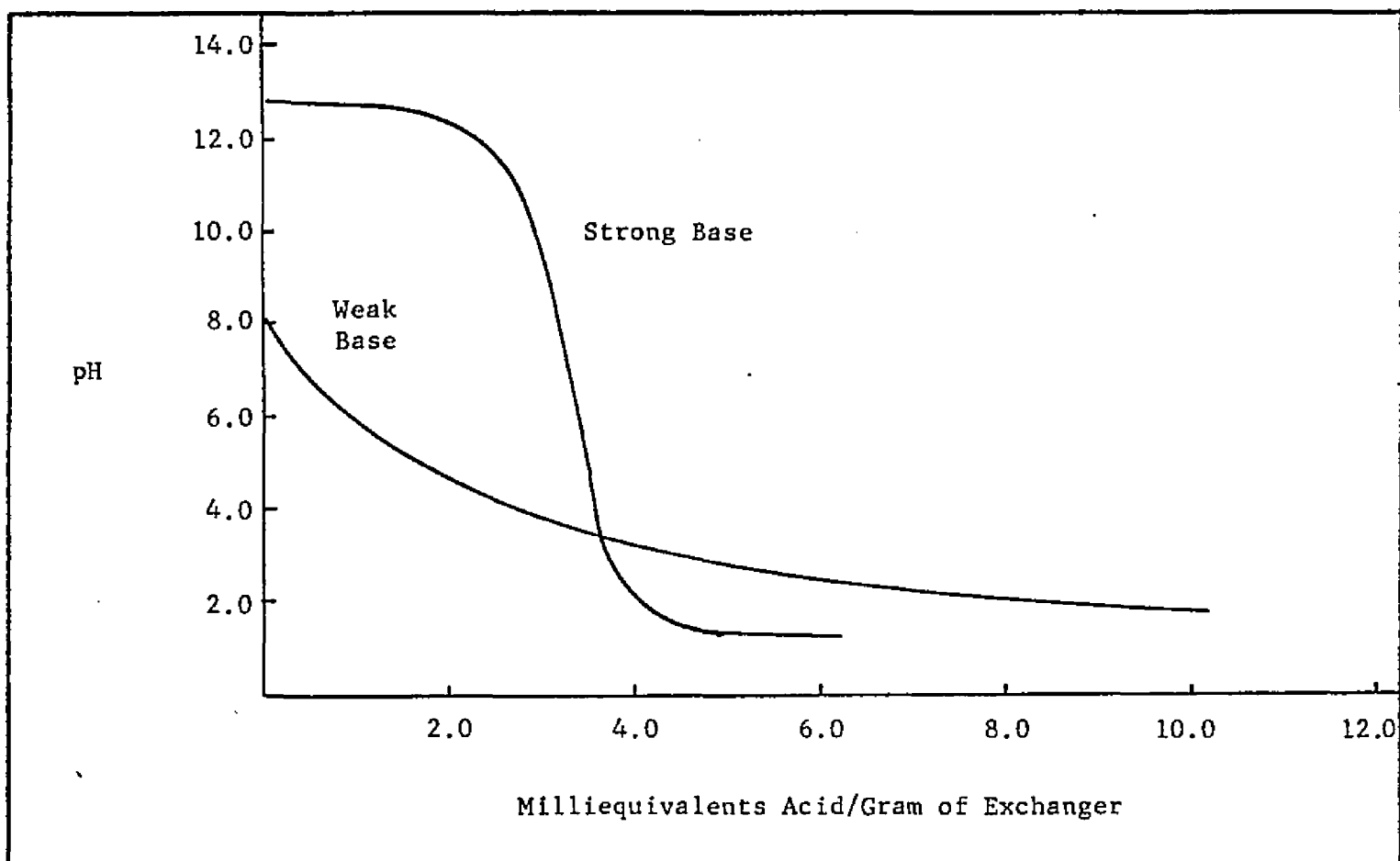
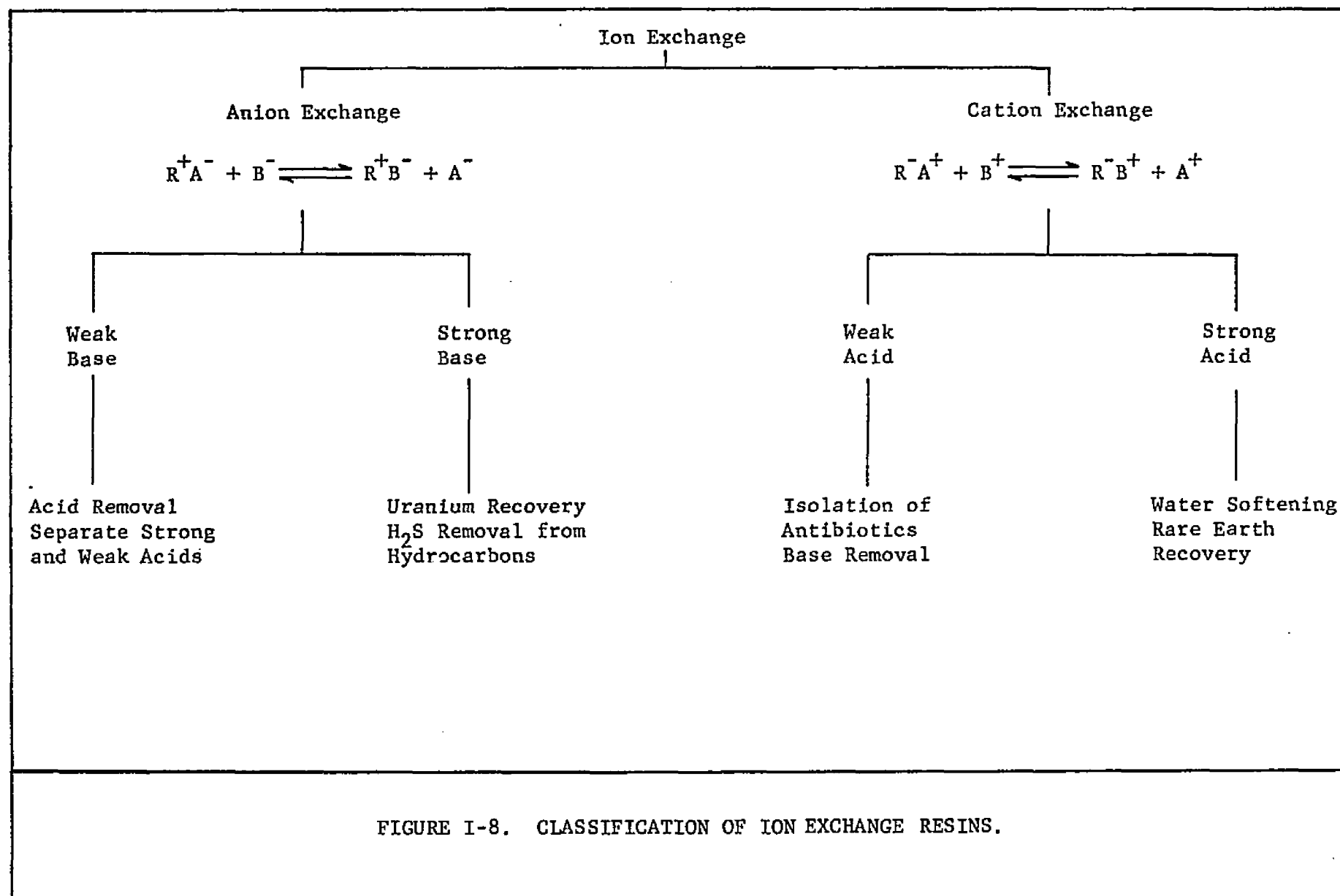


FIGURE I-7. TITRATION CURVES OF ANION EXCHANGE RESIN.



"bead" polymerization, they are used in the bead form. This form has several hydrodynamic advantages over other forms but usually are not as porous and have less surface area than other forms. There has been some research in the area of ion exchange membranes as well as ion exchange papers, pulps and yarns.

Most of the research on ion exchange has been devoted to finding new ionogenic groups and to finding new substrates for the attachment of these groups. One of the reasons for this has been the hope that new types of ionogenic groups will allow some previously inseparable materials to be easily separated. New substrates have been investigated primarily so that new resins may be developed which can withstand harsher environments.

#### Ion Exchange Derivatives of Cellulose

The use of cellulose as the polymeric substrate to which ionogenic groups are attached offers several important advantages. Because of its carbohydrate nature, it is hydrophilic. The advantages of this type of substrate were discussed in the preceeding section. Guthrie and Bullock (58) point out several additional qualities ion exchange have. They are much finer than ordinary ion exchange resins and thus possess a larger surface area. Their open, porous structure permits the entrance or attachment of large molecules which cannot readily be absorbed by other types of resins. The rate of exchange of ions with cellulosic exchangers is so rapid no kinetic measurements of exchange can be made with them as with other types of resins. Ion exchange celluloses are extremely versatile as to the form in which they are used and the choice can be made between a fabric, a yarn, a fiber, a pulp or a paper depending on the application.

Some of the more important cationic ion exchange celluloses and their methods of preparation are shown in Table I-7. All of the cationic ion exchange celluloses derive their ion exchanging ability from an acidic hydrogen attached to the cellulose substrate. The mechanism for exchange is illustrated in Equation (I-10) using partially carboxymethylated cellulose as an example.



The versatility available as to which type of acidic functionality, i.e. strong or weak, the ion exchange cellulose can have should be noted.

Table I-8 give the more important anionic ion exchange cellulose along with a brief description of how they are made. The exact nature of some of these exchangers is not well established with the major controversy being over the question of whether or not a given treatment of a tertiary amine weak base exchanger produces the quaternary ammonium salt. If such a group is formed the exchanger changes from a weak base to a strongly basic anionic ion exchanger. Benerito, Woodward and Guthrie (66) point out the fact that some of the anion exchangers reported to be a quaternary salt are in truth still in the unquaternized form. However, they give conditions under which some of the weak base materials may be quaternized. The conditions given are quite stringent, requiring close control of reaction conditions. McKelvey and Benerito (64) report that commercially available ECTEOLA-cellulose is not in a quaternary form even though such a form is claimed by suppliers. The quaternary can be obtained only



TABLE I-7

## CATIONIC ION EXCHANGE CELLULOSES

Exchanger	Reactants for Synthesis
Carboxymethyl Cellulose	Monochloroacetic acid in presence of NaOH (59, 60)
Phosphorylated Cellulose	Phosphoric acid and urea (61)
Sulfoethylated Cellulose	2-chloroethylsulfonic acid in presence of NaOH (62)
Succinic Half Ester of Cellulose	Succinic anhydride in pyridine (63)

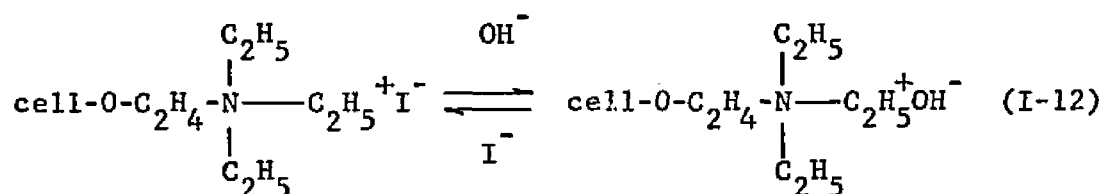
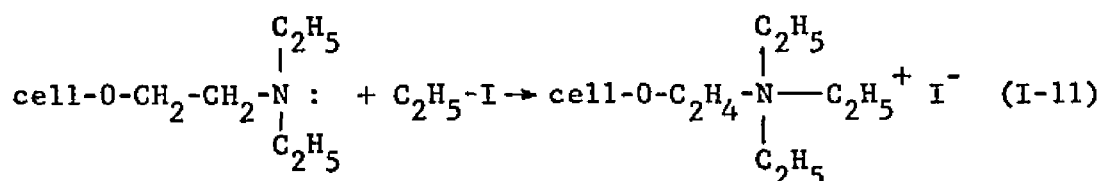
TABLE I-8

## ANIONIC ION EXCHANGE CELLULOSES

Exchanger	Reactants for Synthesis
ECTEOA-Cellulose	Mixture of epichlorohydrin and tri-ethanol amine (64)
DEAE-Cellulose	2-chloroethyl diethyl amine (65)
TEAE-Cellulose	DEAE cellulose and ethyl bromide (65)

by adjusting the reactant ratio. Further study of the actual reaction mechanism involved in the quaternization of triethanol amine and triethylamine has also been carried out by McKelvey, Benerito and Ward (67).

McKelvey and Benerito (64) also report that commercially available TEAE-cellulose is claimed to be a quaternary anion exchanger (68), yet their data shows that it behaves more like the weakly basic form of DEAE-cellulose which may only be quaternized by proper treatment with either methyl iodide or ethyl bromide. The mechanism by which the quaternary salt is formed is demonstrated in Equation (I-11) and the mechanism of anion exchange by quaternary salts is shown in Equation (I-12).



The development of ECTEOLA-cellulose by Sober and Peterson (56, 57) opened up a new field for ion exchange in general and for cellulose ion exchangers in particular. Their work demonstrated that proteins, enzymes, nucleic acids and other biological chemicals could be fractionated by this type of exchanger. This piece of work

caused the research on ion exchange cellulose to increase at such a rapid rate that a recent review on the subject (69) referenced some three hundred seventy papers on the subject which have been published since their initial work in 1956.

Ion exchange celluloses do not have values for ion exchange capacities as high as some of the resins with other substrates. This is because of the degradation which occurs during most cellulose reactions when the degree of reaction is carried to a high level. However, the work by Sober and Peterson demonstrated the usefulness of resins with high surface areas such as are possessed by cellulosic ion exchangers. Table I-9 gives the reported levels for cation exchange capacities and Table I-10 gives the same information for anion exchanging resins.

TABLE I-9  
CAPACITIES OF CATION EXCHANGE MATERIALS

Exchanger	Capacity (meg/gram)		
Carboxymethyl Cellulose	0.7 <sup>(64)</sup>	0.3 <sup>(70)</sup>	0.7 <sup>(58)</sup>
Carboxymethyl Cellulose	0.7	--	--
Carboxy Cellulose	0.7	--	--
Phosphorylated Cellulose	0.8	1.3 first hydrogen 2.6 second hydrogen	1.3
Sulfoethylated Cellulose	0.4	0.5	0.5
Partial Succinic Half-Ester	--	0.3	1.0
Sulfonic Acid Resin	--	---	4.2
Carboxylic Resin	--	--	10.0

TABLE I-10  
CAPACITIES OF ANION EXCHANGE MATERIALS

Exchanger	Capacity (meg/gram)			
DEAE-Cellulose	.81 <sup>(66)</sup>	1.0 <sup>(64)</sup>	0.3 <sup>(70)</sup>	0.7 <sup>(58)</sup>
TEAE-Cellulose	.51-.59	1.0	--	0.7
ECTEOA-Cellulose	.15	0.5	--	0.4
DEAE-Cellulose: CH <sub>3</sub> I	.72-.77	--	0.3	--
DEAE-Cellulose: C <sub>2</sub> H <sub>5</sub> Br	.69-.77	--	--	--
Aminized Cotton	--	--	0.6	--
Weakly Basic Resin	--	--	--	10.0
Strongly Basic Resin	--	--	--	4.0

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## CHAPTER II

### EXPERIMENTAL APPARATUS AND PROCEDURES

#### A. Preparation of Reactants

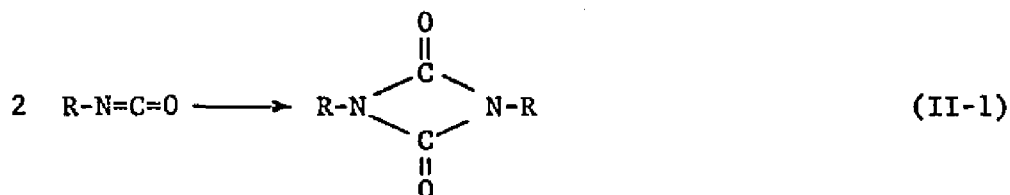
The cellulose used in carrying out this research was purified cotton linters. To ease handling, the linters were ground to pass through a 60 mesh screen. Care was taken to insure that no extraneous materials, such as dirt, grease or oil, was inadvertently mixed with the linters. These linters were then stored in a sealed container until used.

Some of the reactions carried out in this research required that the cotton linters be free from all moisture. In these instances, the linters were dried in a vacuum oven at 90-110°C for four to five hours. Usually, a slight air bleed to the oven was maintained so that moisture removed from the linters could be swept from the system. Even so the pressure in the oven was kept at less than two mm. of mercury absolute. An alternate method of drying was used in which no bleed was allowed, but anhydrous phosphorous pentoxide was placed in the oven. Both methods proved satisfactory with neither showing any advantages over the other. When the cotton linters were dry, they were removed from the oven and stored in a desiccator over phosphorous pentoxide. Phosphorous pentoxide was required because some of the more common desiccants, such as calcium chloride and silica gel, were not adsorbent enough to protect the cellulose from moisture; in fact cellulose often adsorbed moisture from the poorer desiccants. All of

the other drying methods discussed in Chapter I were tried, but they were discarded in favor of this simpler, and in some cases, better procedure.

Solvents used in this research were reagent grade and unless otherwise stated were used as received from the manufacturers.

Reactants were used as received from their manufacturer and were reagent grade with the exception of methylene bis (*p*-phenyl isocyanate). If aromatic isocyanates are stored at room temperature for a month or so they form dimers according to Equation (II-1). To return them to



the monomeric form it is necessary to heat them to the decomposition temperature and remove the aryl isocyanate by distillation under vacuum. Sulfonyl isocyanates do not dimerize and the phenyl isocyanate used was fresh.

To regenerate the methylene bis (*p*-phenyl isocyanate) a 100 milliliter round bottom flask was filled with granules of the dimer. A Claissen head, air condenser, and vacuum take-off connected to a 100 ml. receiver was then placed on the flask. A high vacuum, approximately 2.0 mm of mercury absolute, was drawn on the system. The flask was then immersed in a hot silicon oil bath at 235°C resulting in a simultaneous melting and decomposition of the dimer. The monomer distilled at 160°C. An equal volume of hexane was added to the monomer. The resulting mixture was heated to reflux to form a solution and

filtered into an equal volume of hexane at approximately 0°C. The hexane solution was then placed in a freezer until the purified monomer crystallized. The crystals were filtered and dried under high vacuum at room temperature. The purified isocyanate monomer had a sharp melting point at 45°C vs. a reported value of 42-43°C.

## B. Reactors Used in the Preparation of Cellulose Derivatives

The reaction of a solid with either a liquid or a gas may be carried out with or without a carrier solvent. These two types of processes require two different reactor types. Both were used in this research.

The reactor used in carrying out reactions on a solvent free basis requires both good mixing and good heat transfer between the solid bulk and the reactor wall. This was accomplished by constructing a reactor whose surface was scraped by a helical screw with teflon blade coverings. The screw was driven by a 3/4 horsepower motor with a variable-drive mechanism. A double mechanical seal was used on the shaft of the screw and a specially designed hydraulic piston arrangement was used to keep the oil pressure in the mechanical seal chamber always a little higher than the pressure in the reactor.

Reaction temperatures were maintained by passing water or water mixed with steam through the jacket walls of the reactor. Temperature control was provided by a wall mounted Honeywell temperature programmer which regulated the amount of steam mixing with a fixed flow of water. A special safety system was arranged so that if an abnormal rise in temperature occurred the jacket wall would be flooded with water. As an extra precaution a blowout valve was attached to a one half inch line leading up through the roof and outside of the building.

Solids were loaded by removal of the blind flange on the end of the reactor. Liquids and gases were added to the system from weighed lecture cylinders by pressuring them into the reactor through a special spring loaded spray mechanism; giving a uniform distribution of these reactants over the tumbling cotton linters.

The reactors utilizing a carrier solvent have less critical requirements because of better heat transfer and more uniform mixing. Reactors used in this category included a heavy-glass four liter reactor, a series of multi-neck round-bottom flasks, and a series of sealed reactors.

The heavy-glass reactor was equipped with propellor type mixers driven by an air motor. The reactions carried out in this reactor called for the use of sodium hydroxide so that the cooling coils and all other fittings in the reactor were monel. Temperature and pressure control systems were essentially the same as for the scraped surface reactor. Solids were added to the reactor through a one inch nozzle on the reactor head. Liquids could be added from an external supply through a valve on the reactor head. To assure that reactant gases would receive adequate mixing, a dip leg extending to a point below the bottom propellor was installed. Thus the reactor was developed to be as versatile as possible.

A series of reactors, consisting of various sizes of round-bottom flasks were also used in this research. These flasks were usually 500-1000 ml in size and had four necks with 24/40 ground glass joints. The center neck was equipped with an air driven motor and glass stirring rod having teflon blades fitting the contour of the flask. A pyrex dropping funnel was placed in another neck for the addition of liquids. When gases were added to the system, a fritted glass sparger was used in place of the funnel. If the reaction was run at reflux conditions another neck was fitted with a water cooled reflux condenser while at other times this neck was occupied by a thermometer. The last neck was arranged so that a positive nitrogen pad could be kept

on the system. This was accomplished by an arrangement such as shown in Figure II-1. Nitrogen was fed to a glass tee, one branch of which went to the reactor and the other branch led to a bubbler filled with glycerin insuring a slight positive nitrogen pressure in the reactor.

Temperature control was maintained by heating mantles connected to variacs. In systems forming a viscous solution it was found that better temperature control with less polymer degradation could be maintained by using an oil bath for heating rather than the heating mantels.

A series of sealed reactors provided small anhydrous systems for rapid evaluation of reaction conditions. These reactors were 15 and 50 milliliter screw top pyrex test tubes, and 150 and 250 milliliter beverage bottles. The beverage bottles were sealed with standard caps fitted with rubber septums using a hand bottle capper.

Reaction temperatures for these systems were controlled by immersing the sealed reactors in a large constant temperature oil bath. Mixing was done by manually shaking the reactors at frequent intervals during the course of a reaction.

### C. Procedures Used in the Preparation of Cellulose Derivatives

#### Carboxymethyl Cellulose

There were two different procedures used in forming carboxymethyl cellulose in this research. One was a modification of the laboratory method proposed by Klug (1) and was carried out in the 4 liter heavy glass reactor. The other was a procedure requiring no solvent carrier using the scraped surface reactor.

A typical feed charge to the glass bottom reactor is shown in Table II-1 while typical reaction conditions in this reactor are given in Table II-2. Cotton linters and isopropyl alcohol were loaded into the reactor through the nozzle in the reactor head. The blind flange covering the nozzle was fastened in place and mixing begun. After a uniform slurry of cotton linters had been formed a vacuum was drawn on the reactor. Sodium hydroxide was added from a dropping funnel attached to the reactor head by one quarter inch monel tubing. The caustic flow rate was kept very slow so that no temperature rise occurred because of caustic addition. Water was circulated through the coils to keep the temperature from rising during caustic addition. Mixing at room temperature was continued for two to two and one-half hours for alkali cellulose formation to be complete and uniform.

At this point the controller cam was set at 40°C. When the reactor temperature had leveled out, addition of monochloroacetic acid was begun. The addition was very slow and was stretched over an hour long period. Approximately three hours were allowed for complete reaction of monochloroacetic acid.

To purify the carboxymethylated derivative from this process the contents of the reactor were filtered through a Buckner funnel. The



TABLE II-1

TYPICAL FEED CHARGE TO ONE GALLON GLASS REACTOR  
USED IN MAKING SODIUM CARBOXYMETHYL CELLULOSE

Reagent	Form	Weight Added (Grams)	Mole Ratio Compared to Cellulose	Volume Added (ml)
Cellulose	ground cotton linters	40.5	1.0	--
Sodium Hydroxide	as a 50% water solution	64.0	6.4	--
Monochloro- acetic Acid	as a 50% water solution	70.9	3.0	--
Isopropyl Alcohol	liquid	--	--	1700

TABLE II-2

TYPICAL REACTION CONDITIONS IN FORMING  
SODIUM CARBOXYMETHYL CELLULOSE

Temperature - 40°C

Pressure - atmospheric; vacuum while adding monochloroacetic acid

Time - 3 hours from final addition of monochloroacetic acid

Agitation - mixture was kept well stirred throughout reaction

recovered solids were then immersed in isopropyl alcohol and excess caustic was neutralized with hydrochloric acid. Solids were again recovered in a Buchner funnel followed by several washings in either a 70:30 isopropyl alcohol-water mixture or a 90:10 acetone-water mixture.

A similar procedure was used in forming carboxymethyl cellulose in the scraped surface reactor; the primary difference being that no carrier solvent was used. In this technique cotton linters were added to the reactor by removal of the end flange. After replacing the flange and pressure testing the reactor, oxygen was removed from the system by repeatedly drawing a vacuum and then replacing the vacuum with nitrogen pressure. A 20 psia nitrogen pad was left on the system. Water was started through the reactor jacket and mixing of the cotton linters begun. A 50 percent aqueous solution of sodium hydroxide was pressured into the reactor from a monel weighing cylinder. After two hours of mixing, monochloroacetic acid was added to the alkali cellulose. The desired reaction temperature (about 25°C) was then set on the controller and held for the duration of the reaction. Purification of the product was similar to that previously discussed.

The product from both of these reactor systems is actually the sodium salt of carboxymethyl cellulose. For ion exchange work the acid form is desired and can be obtained by the method of Eyler, Klug, and Diephuis (2). This is essentially the method used to regenerate the acid form of cation exchange resins. It requires soaking sodium carboxymethyl cellulose in an acid solution of  $\text{pH} \leq 1.0$  for several hours. The excess acid is then washed away in repeated rinses with distilled water.

### Cellulose Phenyl Carbamate

Cellulose phenyl carbamate is the reaction product of cellulose and phenyl isocyanate. The mechanism of this reaction was described in Chapter I along with some of the past work done on reacting isocyanates with cellulose.

Because of the reactivity of isocyanates with moisture, all weighings and transfer of reagents were carried out in a nitrogen padded system. All glassware was dried in a vacuum oven. This included a round bottom flask, used as the reaction vessel, four ground glass stoppers and a stoppered dropping funnel. These along with the necessary reagents were placed in a dry box for loading.

A typical feed charge used in this reaction is given in Table II-3 and typical reaction conditions in Table II-4. The zinc chloride: pyridine complex shown in the feed charge was used to disrupt cellulose crystallinity and was prepared in the reactor by adding 10.75 grams of pyridine to 9.25 grams of zinc chloride while stirring with a nickel spatula. After the complex was formed, pyridine and the cotton linters were added to the reactor forming a slurry. The reaction flask was then sealed with the ground glass stoppers which had been well-lubricated with stopcock grease. Phenyl isocyanate was loaded into the dropping funnel and sealed.

Both the stoppered reaction flask and the dropping funnel were removed from the glove box and as rapidly as possible one of the ground glass stoppers was removed from the flask and the nitrogen pad established by inserting the ground glass fitting as shown in Figure II-1. The nitrogen pad was regulated by bubbling a stream in a branch line through glycerine. When this arrangement was completed, the other

TABLE II-3

TYPICAL FEED CHARGE FOR FORMATION OF PHENYL  
CARBAMATE DERIVATIVE OF CELLULOSE (3)

Reagent	Form	Weight (Grams)	Volume (ml)
Cellulose	ground cotton linters	5.0	--
Phenyl isocyanate	liquid	15.0	--
2 mole pyridine:1 mole ZnCl <sub>2</sub> complex	solid	20.0	--
Pyridine	liquid		150
Dibutyltin dilaurate	liquid		1

TABLE II-4

TYPICAL REACTION CONDITIONS FOR FORMATION OF  
PHENYL CARBAMATE DERIVATIVE OF CELLULOSE

Temperature - 119°C (reflux)

Pressure - under a nitrogen pad, only very slight positive  
pressure

Time - 16 to 18 hours from addition of phenyl isocyanate

Agitation - mixture was kept well stirred even though it  
became very viscous as the reaction proceeded.

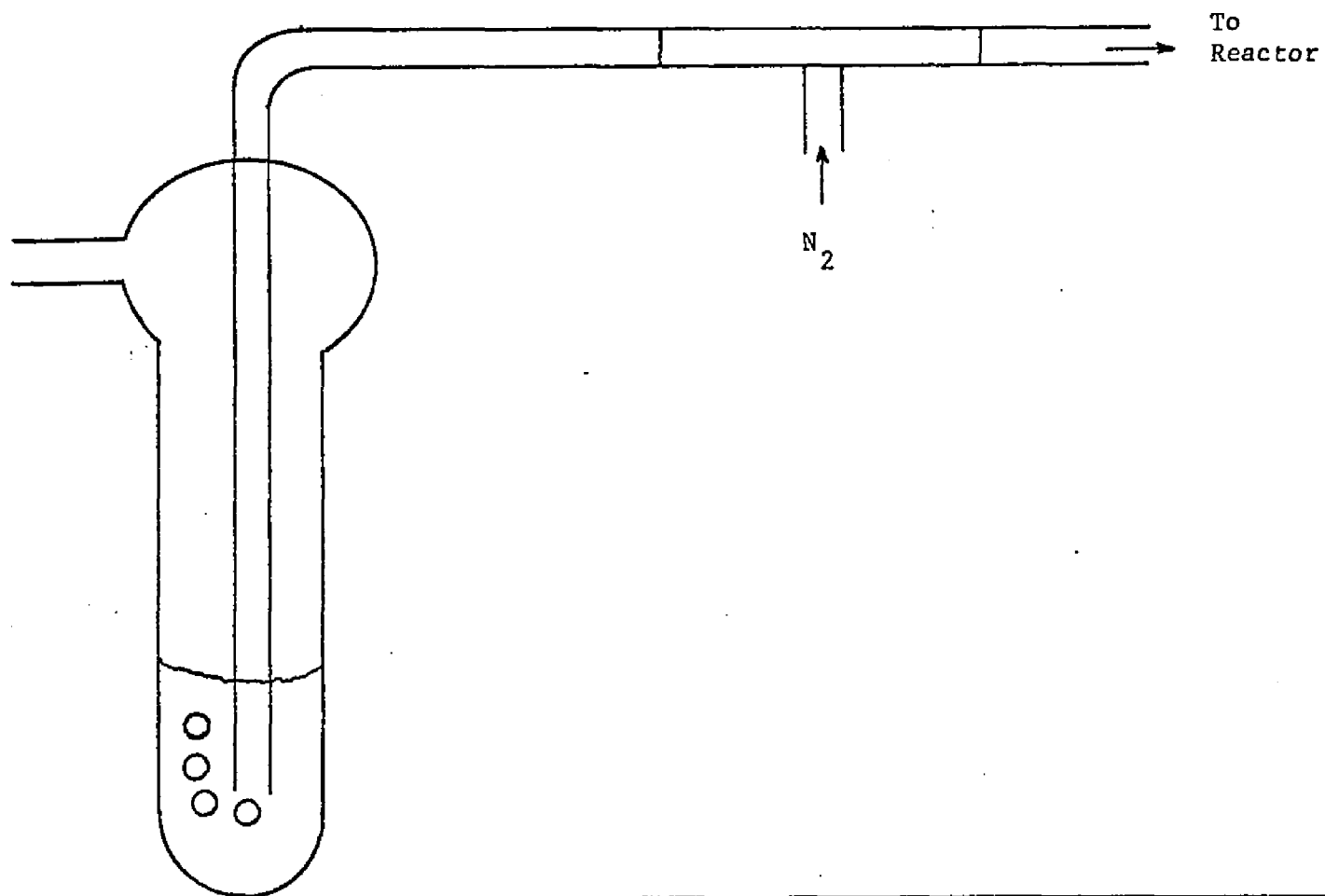
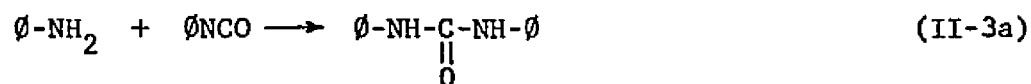
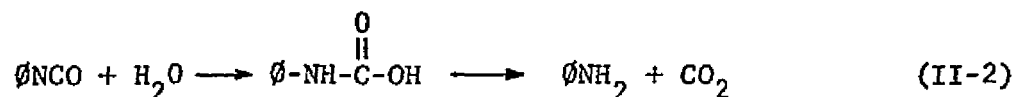


FIGURE II-1. NITROGEN PADDING APPARATUS  
FOR BATCH REACTOR.

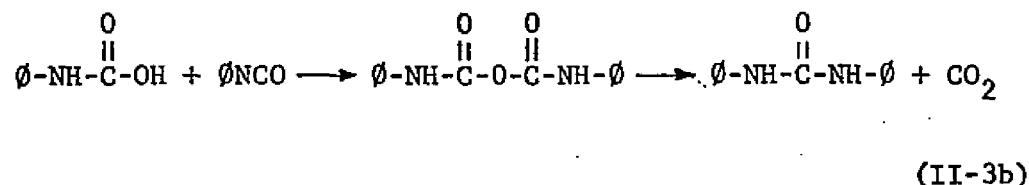
stoppers were replaced with a glass stirring rod, dropping funnel, and reflux condenser. This entire operation was carried out as rapidly as possible to minimize contamination by atmospheric moisture.

Stirring was begun and the heating mantle turned on. After the system was brought to reflux (requiring approximately 30 minutes), the phenyl isocyanate was added. Dibutyl tin dilaurate, a common catalyst for isocyanate reactions, was injected into the reactor. The reaction conditions were held for 16 to 18 hours before the heat was turned off. During the reaction, the polymer dissolved. The product was isolated by pouring the polymer solution into a high speed blender containing about 600 milliliters of ethyl alcohol.

Ethyl alcohol was chosen as a precipitant, not only because it is a non-solvent for the cellulose derivative but also because it dissolves the by-product formed by reaction of the isocyanate with moisture as shown in Equations (II-2) and (II-3).



or



After complete precipitation the solid polymer was filtered in a Büchner funnel. It was then refluxed in approximately 250 milliliters

of ethanol and filtered. Finally it was washed in water, filtered and dried under vacuum for 5-6 hours at 80°C. The yield for charge shown in Table II-3 was 16.0 grams of solids.

#### Cellulose p-Toluene Sulfonyl Carbamate

The first successful synthesis of this derivative was accomplished with the same reactor and experimental technique described for the reaction of phenyl isocyanate with cellulose using the feed charge shown in Table II-5. After proving that this derivative could be formed an

TABLE II-5			
TYPICAL FEED CHARGE FOR FORMATION OF PARA TOLUENE SULFONYL CARBAMATE DERIVATIVE OF CELLULOSE			
Reagent	Form	Weight (grams)	Volume (ml)
Cellulose	dry cotton linters	4.0	--
ZnCl <sub>2</sub> :pyridine*	--	16.0	--
p-toluenesulfonyl isocyanate	liquid	20.45	--
pyridine	liquid	--	300
* This complex consisted of 7.4 grams ZnCl <sub>2</sub> and 8.6 grams of pyridine. It was used in initial runs although later it was shown that it was not needed.			

extensive study on variables effecting the reaction was begun. It was immediately learned that the ZnCl<sub>2</sub>: pyridine complex was not needed for this system and all subsequent runs were made without it even

though the other reactant quantities may be held as stated. The viscous solution formed in this reaction resulted in poor temperature control when using a heating mantel and charring of the polymer in hot spots was common. To remedy this a constant temperature oil bath was used, holding the temperature to approximately  $\pm 1^{\circ}\text{C}$  of the desired reaction temperature.

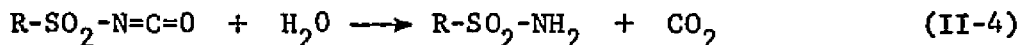
Variables such as reaction temperature, reaction time, etc. were investigated in a series of sealed reactors. A typical procedure using the equipment went as follows: A 50 ml test tube was flamed out under vacuum and placed in a dry box. Dried cotton linters (0.4 grams) were added to the test tube. Thirty-five milliliters of pyridine were added and 1.46 milliliters of p-toluene sulfonyl isocyanate were injected from a hypodermic syringe. The test tube was sealed, removed from the dry box, and placed in a constant temperature oil bath at  $80^{\circ}\text{C}$ . The reaction was run for about six hours. The polymer was precipitated in a high speed blender containing 400 milliliters ethanol acidified with 10-12 milliliters of 37 percent HCl and was filtered and rewashed in the blender with both ethanol and water. The collected polymer was dried under vacuum at  $80^{\circ}\text{C}$  for 5-6 hours. A degree of substitution of 2.25 was attained for this feed charge and reaction conditions.

The ethanol was made acidic to aid in extracting pyridine from the polymer. Acetic acid was also used but was harder to wash from the recovered cellulosic. Refluxing the recovered derivative to remove the side product from reaction of the sulfonyl isocyanate with moisture is not required because rather than forming a urea, sulfonyl isocyanates react, as in Equation (II-4), with moisture to give the



corresponding sulfonamide.

The *p*-toluenesulfonamide is more soluble in ethanol than the urea would be.



To aid in forming a more uniform precipitate, extremely viscous solutions were diluted with equal volumes of pyridine or dimethyl sulfoxide before precipitation. Dimethyl sulfoxide is remarkably effective in reducing the apparent viscosity; only 10 cc. are required to provide a free flowing solution of 2 g. of cellulose derivative dissolved in as little as 15 m. of pyridine.

#### Crosslinking Reactions

Various crosslinking techniques and reagent were studied in this research. In general, the crosslinking of the cellulose derivative was carried out directly in the system used to synthesize the derivative. An exception to this was the crosslinking of films cast from polymer solutions.

Cellulose *p*-toluenesulfonyl carbamate was crosslinked in approximately 1-2 percent solutions in pyridine. Some of the reagents used for this purpose were methylene bis (*p*-phenyl isocyanate), chlorosulfonyl isocyanate, *p*-isocyanatophenylsulfonyl isocyanate, dichloroacetic acid, and trichloroacetic acid. A typical procedure required formation of the solution and addition of approximately 0.15 mole of crosslinking reagent per moles of cellulose. The system was then heated to about 80°C for 6-10 hours. A gradual thickening of the solution occurred, until finally the solution had formed a thick gel.

Purification of the crosslinked polymer required vigorous grinding of the gel in a blender with acidic ethanol solutions, prepared as previously described. After rinsing the crosslinked polymer in ethanol and water, again with vigorous mixing in a blender, the collected resin was dried for 6-10 hours under vacuum at about 80°C.

Some work was done on crosslinking films cast from pyridine solutions of cellulose p-toluenesulfonyl carbamate. To do this the film was air dried for only two to three hours, so that it still contained a relatively high percentage of pyridine. A section of about two inches by four inches and approximately .002 inches thick was loosely wrapped around a glass rod. The rod was placed in a 50 milliliter test tube, if a solvent carrier was used (such as benzene) about 15-20 milliliters were added, followed by the crosslinking reagent. The test tube was placed in a constant temperature bath at 80°C for 10-12 hours. The films were removed from the test tubes, rinsed with benzene and air dried. The dried films were brittle and opaque.

### C. Analytical Procedures

The analysis of the cellulose derivatives produced by the aforementioned techniques took two classical approaches. Initial analytical work on a sample was qualitative in nature, then if it seemed that the detail, time, and trouble of a quantitative analysis were required, one was performed. Qualitative analysis could be carried out using infrared spectroscopy, while the quantitative work was accomplished using both classical chemical techniques as well as nuclear activation analysis.

#### Qualitative Analysis for Substituent Groups on Cellulose

Infrared analysis was obtained using a Beckman IR 8. Spectra were run using one of three procedures. If the sample could easily be dissolved in a non-interfering solvent, the spectrum was run by injecting a solution of the sample into sodium chloride cells. Solid samples were analyzed using a potassium bromide pellet technique. The third method for preparing samples for infrared analysis was used when a film could be produced from solutions of the cellulose derivative. Here there were two techniques used in obtaining these films. In one method an eye dropper was used to place a few drops of a polymer solution on a sodium chloride plate. The film was formed by placing the plate in close proximity to a light bulb and evaporating the solvent. Alternatively, the film could be cast on a glass plate, dried, and stripped off.

#### Quantitative Analysis for Degree of Substitution

The number of pendent groups attached to each anhydroglucose unit was determined by quantitatively analyzing for a particular characteristic of these groups. These types of analysis assume that

the derivative is fairly uniformly substituted and the results can be translated from such terms as weight percent of an element into degree of substitution.

A close approximation to the degree of substitution can be obtained from the weight gain of the polymer. This requires that the polymer be thoroughly washed and dried after reaction. Inasmuch as cellulose is such a strong adsorbent of moisture, the initial weight must also be determined under anhydrous conditions.

#### I. Apparatus Required

- A - resealable reaction vessels
- B - single beam balance
- C - dry box
- D - Mettler balance accurate to .1 milligram

#### II. Procedure

The reaction vessel is thoroughly dried by one of the earlier described procedures. A tare weight of the reactor is taken with the Mettler balance. The reaction vessels are placed in the dry box and loaded with cellulose which has previously been dried and weighed out on the single beam balance contained in the dry box. The sealed reaction vessels are then removed from the dry box and weighed on the Mettler balance for a precise determination of the amount of cellulose being reacted. After the reaction had been completed and the products had been carefully washed and dried, their weight is again determined.

#### III. Calculations

The degree of substitution is calculated from weight gain as follows:

$$\text{Weight gain} = \text{Final Weight} - \text{Initial Weight of Cellulose}$$

$$\text{Moles of Substituent Added} = \frac{\text{Weight Gain}}{\text{M. W. of Substituent}}$$

$$\text{D. S.} = \frac{\text{Moles of Substituent Added}}{\text{Initial Weight/M. W. of Cellulose}}$$

A more sophisticated approach was used in later analytical work which involved analyzing for an element in the final product which was present only in the substituent group and not in the substrate. Carbamate derivatives of cellulose had nitrogen atoms present which met these requirements and sulfonyl carbamates had both nitrogen and sulfur available. Initial work on nitrogen analysis using the standard Kjeldahl method gave results which did not correspond to weight gain analysis. It was later learned that the materials being analyzed required a predigestion reduction step using hydroiodic acid or zinc and HCl. Because of this, sulfur analysis was used for determination of degrees of substitution of the sulfonyl carbamates. The standard Schoniger (4) method as described by Steyermark (5) was used for this analysis.

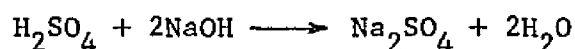
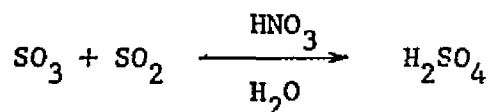
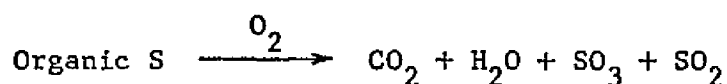
#### I. Reagents Requires

- A - approximately .01N NaOH
- B - approximately .1N NaOH
- C - approximately .01N HCl
- D - approximately .1N HCl
- E - fuming nitric acid
- F - tetrahydroxyquinone indicator (THQ)
- G - standard .01N barium chloride
- H - phenolphthalein

#### II. Apparatus Required

- A - combustion flask
- B - filter paper carriers
- C - burette
- D - Erlenmeyer flask

### III. Reactions



### IV. Procedure

The sample is weighed onto the filter paper carrier which is then folded and inserted on the platinum gauze basket attached to the combustion flask. 10 ml of approximately 0.01N NaOH are added to the flask which is then flushed with oxygen. The paper is ignited and immediately inserted into the oxygen filled flask. The flask is held inverted until the combustion is completed. It is then cooled for about one minute before the contents are shaken vigorously for the cloudiness to disappear. A few milliliters of water are then placed in the cup surrounding the stopper and the flask is let sit for about 15 minutes for complete absorption of the oxidation products. The contents are then transferred to a beaker along with one milliliter of fuming nitric acid. The solution is then evaporated to dryness. The residue is dissolved in water. After a few drops of phenolphthalein indicator are added, the solution is made alkaline with approximately 0.1N NaOH. It is then back titrated with approximately .01N HCl just to expel the color. An equal volume of ethanol is then added, followed by a slight amount of powdered THQ. The solution is then titrated with barium chloride, 0.01N, to the reddish-purple endpoint.

## V. Calculations

1 ml of 0.01N BaCl<sub>2</sub> is equivalent to 0.1603 mg of sulfur

$$\% \text{ sulfur} = \frac{(\text{ml. of 0.01N BaCl}_2)(0.1603)}{\text{wt. of sample}} \times 100\%$$

$$\text{D. S.} = \frac{162 (\text{wt. fraction sulfur})}{32.0 - 197 (\text{wt. fraction sulfur})}$$

### Example

2.16 ml. of 0.01N BaCl<sub>2</sub> is required to titrate the sulfate resulting from the combustion of a 2.960 mg sample

$$\% \text{ sulfur} = 11.7\%$$

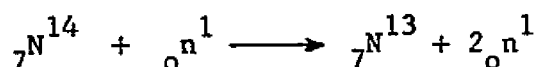
$$\text{D. S.} = 2.12$$

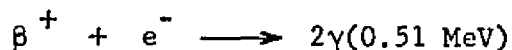
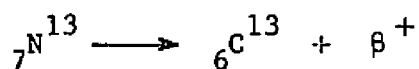
Because of the need for a more rapid analysis of the sulfonyl carbamate derivatives neutron activation analysis for nitrogen content was developed. This procedure is rapid, accurate, and does not destroy the sample. The nitrogen containing materials were bombarded with fast neutrons causing an n, 2n reaction of N<sup>14</sup> to N<sup>13</sup>. N<sup>13</sup> is radioactive and emits a positron on decaying. The positron collides with an electron and their annihilation gives off 0.51 MeV gamma rays. These rays can then be counted and compared with the number emitted by analysis of a standard substance for determination of the nitrogen content of the unknown sample.

## I. Apparatus Required

- A - 2/5 dram flip top vials
- B - fast neutron generator

## II. Reactions





### III. Procedure

A weighed amount of dried sample is added to a 2/5 dram polyethylene flip top vial. The vial is sealed with an electric soldering iron. It is then irradiated for a specified time (15 sec.), allowed to decay for another specified time interval (2 min., 45 sec.), and finally the  $\gamma$  rays are counted over a standard time interval (4 min.). The times shown may vary but must be the same for each sample as well as for the standard.

### IV. Calculations

neutron flux for standard =  $N_S$

neutron flux for unknown =  $N$

photopeak count =  $A$

photopeak count for blank =  $A_B$

normalized photopeak count =  $A^O = A \frac{N_S}{N}$

counts per milligram of nitrogen for standard  $C_S$

milligrams of nitrogen in sample =  $\frac{A^O - A_B}{C_S} = \text{MGS}$

weight percent nitrogen in sample =  $\frac{\text{MGS} \times 100\%}{\text{sample weight}}$

$$\text{D. S.} = \frac{162 (\text{wt. \% nitrogen})}{14 - 197 (\text{wt. \% nitrogen})}$$

Example

$$N_S = 20523$$

$$N = 20404$$

$$A = 2477$$



$$A_B = 200$$

sample weight - 309.3 mgs

$$C_S = 142.2$$

$$A^0 = 2477 \frac{20523}{20404} = 2492$$

$$\text{weight percent nitrogen} = \frac{2492-200}{(142.2)(309.3)} \times 100\% = 5.21\%$$

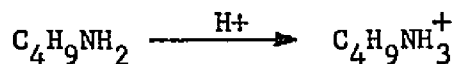
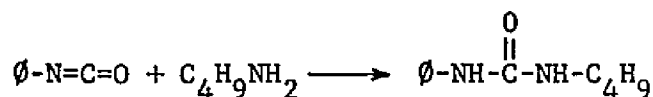
### Analysis for Isocyanates

In the work checking out reaction solvents for the reaction of phenyl isocyanate with cellulose, the possibility existed that the isocyanate was reacting with moisture, that might have leaked into the system, rather than simply not reacting with cellulose. To check this possibility aliquots were withdrawn from the reaction vessel and analyzed for isocyanate using the technique of Siggia and Hanna (6).

#### I. Reagents Required

- A - Butylamine solution. Dilute 25 grams of freshly distilled n-butylamine to 1 liter with dioxane which has been dried over potassium hydroxide pellets
- B- Standard acid (0.1N sulfuric acid)
- C - Methyl red indicator

#### II. Reactions



#### III. Procedure

A sample containing approximately 0.002 moles of isocyanate is weighed in a small glass stoppered weighing bottle. The stopper from the weighing bottle is removed and the weighing bottle containing the sample is placed in a 250 ml Erlenmeyer flask. To the flask are added

20.0 ml of the butylamine solution and the flask is swirled to mix the reactants. For aromatic isocyanates the required reaction time is only a couple of minutes. 25 ml of distilled water are added and the solution is titrated to the methyl red end point with standard sulfuric acid.

#### IV. Calculations

$$\text{total isocyanate present} = .199 (v_A - v_S) N_A \frac{W_T}{W_S}$$

where:

$v_A$  = volume of acid to titrate blank

$v_S$  = volume of acid to titrate sample

$N_A$  = normality of the acid

$W_T$  = total weight of solution

$W_S$  = weight of sample

#### Example

A 3.313 gram sample is removed from a 213.0 gram solution, when 46.8 ml of .101N  $H_2SO_4$  are required to titrate the sample and 64.9 ml are required for a blank

$$\begin{aligned} \text{total isocyanate in solution} &= .119 (64.9 - 46.8) (.101) \frac{213.}{3.313} \\ &= 13.99 \text{ grams total isocyanate present in the system} \end{aligned}$$

#### D. Evaluation of the Properties of Cellulose Derivatives

In any chemical process, one is usually trying to change a chemical substance -- whose physical and chemical properties give it limited utility -- to a material whose properties make it useful in some given application. Consequently, the evaluation of those properties can be almost as important as the actual preparation of the substance being tested. This is especially true in the modification of cellulose. The range over which a given property can change, simply by changing the type and number of substituent groups, has already been illustrated in Chapter I.

##### Solubility

To carry out solubility tests on these polymers, a typical procedure was to place approximately 0.1 gram of the cellulose derivative in a test tube along with 10-15 milliliters of the solvent being tested. The mixture was then shaken intermittently for about 24 hours. Solution was noted by a significant increase in the viscosity of the mixture as well as a disappearance of a major portion of the fibers. If solution does not occur the mixture was heated at 60°C for several hours. The derivative was then classified soluble, swollen (distinct gel-like particles were formed but the overall viscosity of the solvent had not changed), and insoluble.

##### Thermal Properties

One of the methods used in evaluating these properties is known as differential thermal analysis. In this method, the sample and an inert reference substance, undergoing no thermal transitions in the temperature range of interest, are heated at exactly the same rate in

a controlled heater. The temperature difference between the sample and the reference is measured and plotted as a function of sample temperature. A temperature difference is measurable only when heat is being evolved or absorbed because of exothermic or endothermic activity in the sample, or when the heat capacity of the sample is changing abruptly.

The differential thermal analysis work was carried out on a DuPont 900 DTA Instrument. Figure II-2 is a schematic of the sample cell assembly of this instrument. Illustrated in this figure are the block heater, and heating shield, as well as quartz tubes for the sample, reference, and control thermocouples. The entire sample cell is covered by a glass bell jar.

Because of the coarseness of the polymer samples, 4 mm sample tubes were used. These were loaded so that the sample level was approximately 3 mm from the bottom of the tube. Finely ground glass beads were used as the reference substance. The heating rate used was 20 degrees Centigrade per minute and the  $\Delta T$  was set at 2°C per inch. Atmospheric conditions were maintained in the bell jar.

Another piece of equipment used in studying thermal decomposition was a standard tube furnace. Approximately one-half gram of sample was loaded into a pyrex tube, which was then placed under a vacuum so that the absolute pressure was about 2 mm Hg. The lower portion of the tube was placed in the furnace and heated to about 250-275°C. Since the upper portion of the tube was unheated, thermal decomposition products were condensed on this section of the tube forming bands of decomposition products as shown in Figure II-3. The collected products were then analyzed.

A - reference

B - control

C - sample

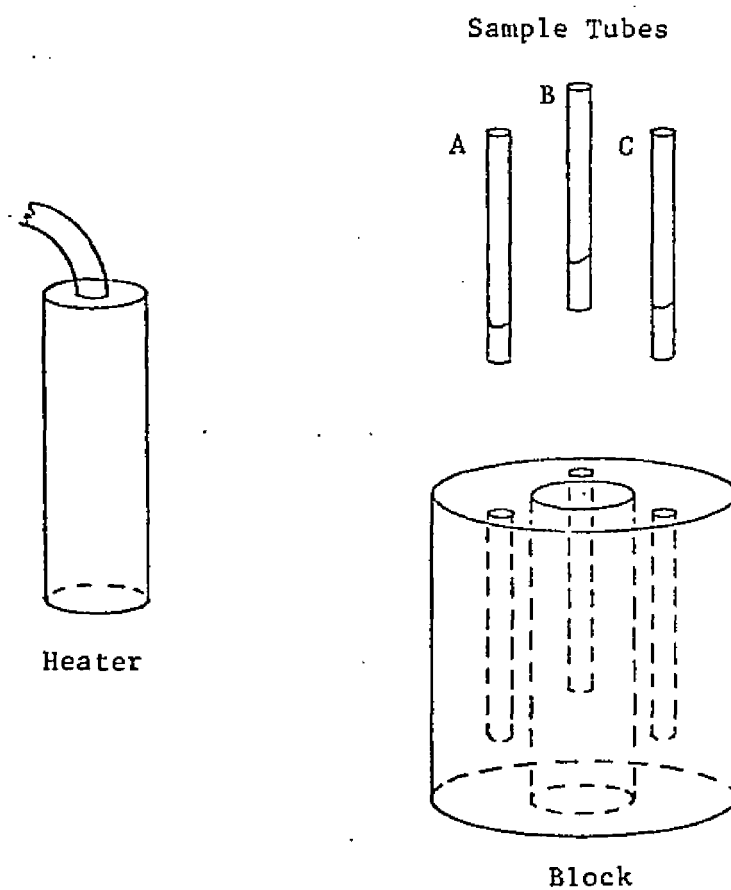
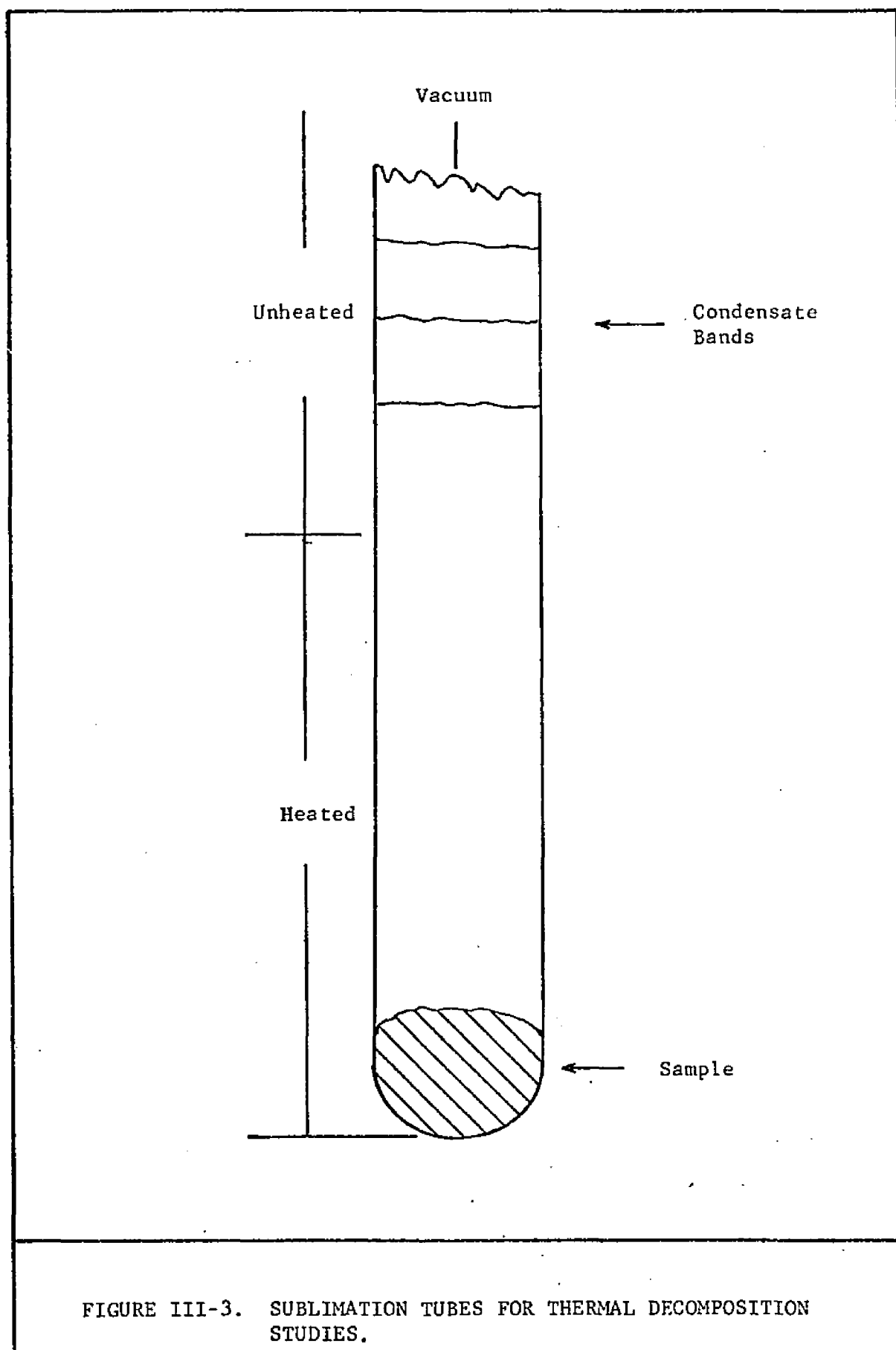


FIGURE II-2. DTA CELL OF DUPONT 900.



## E. Evaluation of the Possible Applications of Cellulose Derivatives

### Ion Exchange

A standard method proposed by Guthrie (7) was used in obtaining ion exchange capacities. To determine the ion exchange capacity of cation exchange resins it is necessary to convert any resins in the salt form to the acid form. This is accomplished by soaking the resin in 5% hydrochloric acid for twenty minutes. The excess acid is removed by repeated washing with distilled water and as is indicated by the development of a pink color on addition of a drop of phenolphthalein indicator and a drop of approximately 0.1N sodium hydroxide solution to 50 ml. of the wash water in which the exchanger has been soaked for about 30 minutes.

After regeneration the ion exchange resins are dried in a vacuum oven. Approximately one gram of the dried resin is then accurately weighed into a glass-stoppered Erlenmeyer flask. Fifty ml of 1 molar sodium chloride solution is added to the flask followed by a measured amount of standard base. The total liquid volume is then brought to 100.0 ml with distilled water. The flasks are allowed to stand, with occasional shaking, for several hours. An aliquot from the supernatant liquid is titrated to the phenolphthalein end point for determination of the cation exchange capacity.

#### Calculations:

meq remaining in solution =

$$\text{ml. of acid for titration} \times \text{normality of acid} \times \frac{\text{total volume of liquid}}{\text{volume of aliquot}}$$

$$\text{meq. initially in solution} = \frac{\text{ml. of base added}}{\text{normality of base}} \times$$

$$\text{capacity} = \frac{\text{meq. initially in solution} - \text{meq. remaining in solution}}{\text{weight of resin in sample}}$$

Example:

sample weight = 1.0370 grams

sodium hydroxide added = 5.0 ml of 2.097N solution

total volume of liquid added - 100.0 ml

hydrochloric acid required for titration = 10.45 ml of  
0.09489N solution

volume of aliquot = 15.0 ml

$$\text{meq. remaining in solution} = (10.45)(0.09489) \frac{100}{15} = 6.6107$$

$$\text{meq. initially in solution} = (5.0)(2.0097) = 10.0485$$

$$\text{capacity} = \frac{10.0485 - 6.6107}{1.0370} = 3.32 \text{ meq/gram}$$

#### Acid Strength of Cation Exchangers

To determine whether a cation exchange material is a strong or weak acid resin, 45.0 ml. of 1 molar sodium chloride solution and 45.0 ml. of distilled water are added to a flask containing a sample of the polymer. The mixture is allowed sufficient time to equilibrate before the pH is measured with a pH meter. Equilibrium is assumed when the pH value is constant on repeated measurement. A measured amount of standard base is added, time is allowed for equilibration and the pH again measured. This process is continued until addition of the base does not change the pH of the mixture. A curve of pH vs. milliequivalents of acid added per gram of dry sample is then plotted. This curve can be compared with the characteristic curves of Figure I-7;



the shape of the curve indicates type of cation exchange resin being investigated.

### Film Casting

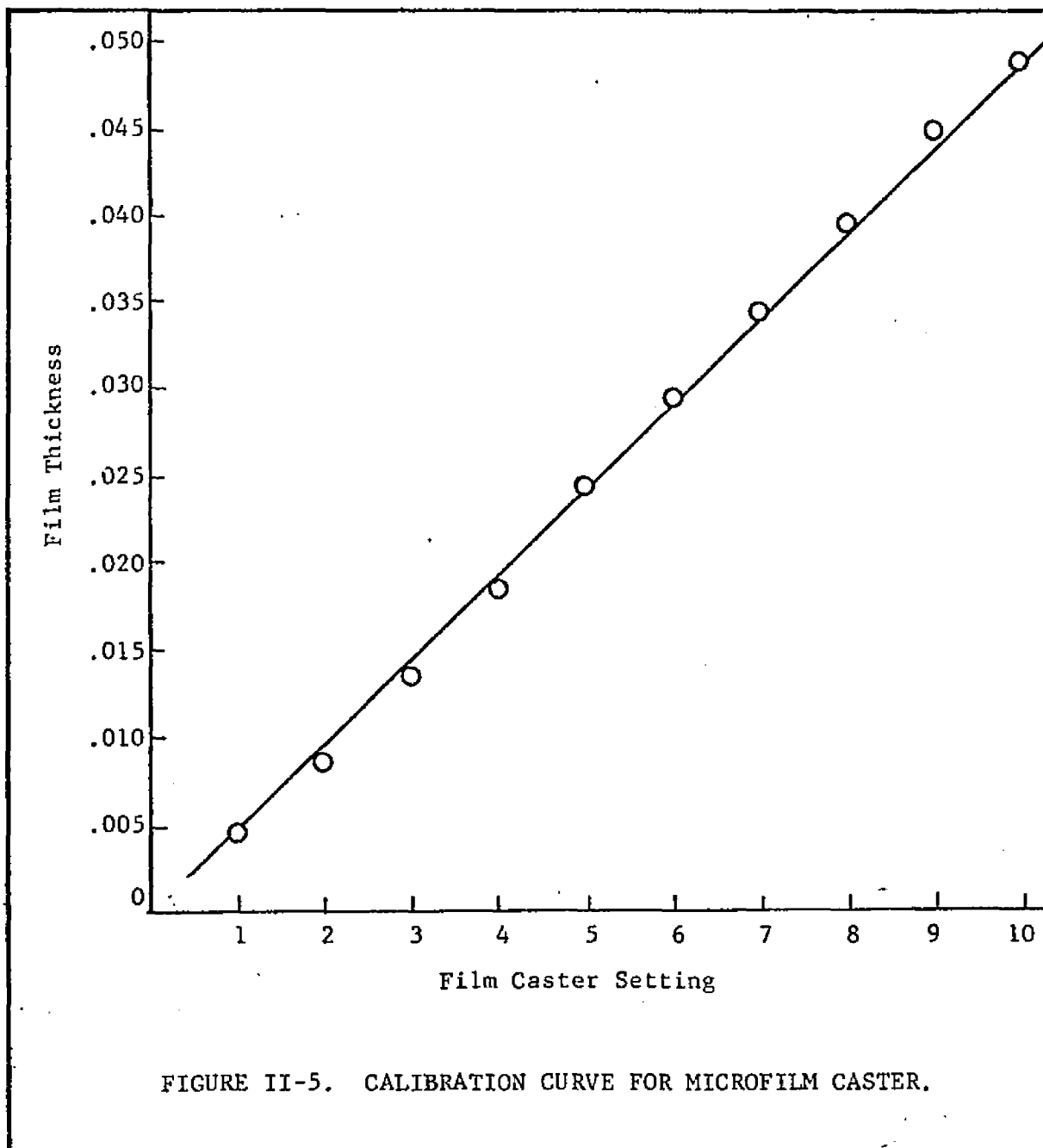
In the reaction of p-toluenesulfonyl isocyanate with cellulose in a pyridine medium, a clear viscous solution is formed. One of the possible advantages to such a reaction system is that films may be cast directly from the reaction mixture. This possibility was investigated using a micro film caster shown in Figure II-4. The thickness of the film laid down by the film caster could be regulated by the calibrated vernier on the device. The calibration curve is shown in Figure II-5.

Before films were cast from the reaction solutions (approximately 1% polymer) all the bubbles in the solution were allowed to escape. The film caster was placed on a freshly cleaned glass plate. The polymer solution was poured into the film caster which was then drawn slowly across the glass plate. Since rapid evaporation of the solvent causes bubbles to be formed in the film, the initial solvent vaporization was done at atmospheric conditions. When most of the solvent has been removed the films were stripped from the plates and cured at slightly elevated temperatures in a vacuum oven.

n-Dibutyl phthalate was used as a plasticizer for these films. To test the effect of this reagent on the film properties it was added directly to the hot pyridine solution (formed during the reaction of p-toluenesulfonyl isocyanate and cellulose) in amounts varying from 0.05 to 0.15 moles of n-butyl phthalate per initial moles of cellulose. The system was shaken to completely mix the plasticizer and then allowed to stand until all the bubbles had escaped before the films were cast.



FIGURE II-4. PHOTOGRAPH OF MICRO FILMCASTER.



### Coating of Carbon Steel

Sulfonyl carbamate derivatives have been shown to have excellent resistance to attack by acid, therefore the possibility of coating low grade metals with these materials was investigated. As in the work on film casting, the coating procedure utilized the solubility of sulfonyl carbamate derivatives in their reaction solvent, pyridine.

Low grade carbon steel strips were sanded with a rough sandpaper, briefly dipped in 1N nitric acid and stored in isopropyl alcohol until ready for coating. On removal from the isopropyl alcohol they were dried with a dry cloth and weighed. Care was taken not to touch the area to be coated with anything but the cloth. After being weighed, the viscous polymer solution was applied by either brushing it on with a small brush or by dipping the metal strip into the solution. The coated strips were then air dried before being cured in an oven. In some instances a second coat was applied after the first had been properly cured. The amount of polymer coated onto the strips was determined by reweighing as well as measuring with a micrometer.

Evaluation of the degree of protection these metals received from the protective coating was accomplished by immersing the strips into various solvents including organics, acids, and bases.

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## CHAPTER III

### DISCUSSION OF RESULTS

#### A. General

As stated in Chapter I, the purpose of this work was to develop a new cellulose derivative which could be used as an ion exchange resin. In this search many possibilities were investigated but the most unique and successful development was the preparation of the sulfonyl carbamate derivatives of cellulose. Of particular interest was the ion exchanging capabilities of these derivatives. Because this was a new polymer, other possible applications of this derivative such as film forming ability, metal coating, fiber formation, and molding ability with epoxy prepolymers were also investigated.

In addition to sulfonyl carbamate derivatives of cellulose, other derivatives were prepared as discussed in Chapter II. Carboxymethyl cellulose was synthesized so that further modifications, such as new procedures of crosslinking could be tried. Cellulose phenyl carbamate was synthesized so that some comparisons could be made between carbamate and sulfonyl carbamate structures and properties.

In Chapter I the difficulty encountered in forming cellulose derivatives was pointed out. Thus it was to be expected that some of the ideas investigated in this research may not work and indeed many of the possibilities explored in the search for new cellulose derivatives were unsuccessful. Discussion of some of these unsuccessful processes are included in this chapter because the principles used in the paper chemistry for the formulation of these derivatives is

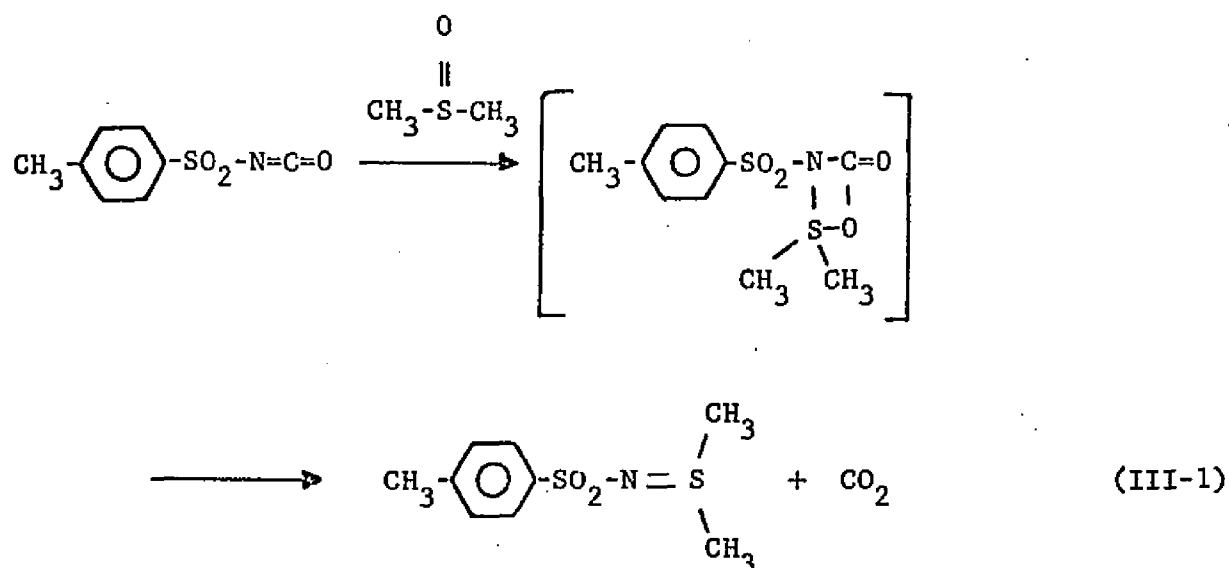
important and because further investigation of these processes may prove to be valuable.

## B. Formation of Cellulose para Toluenesulfonyl Carbamate

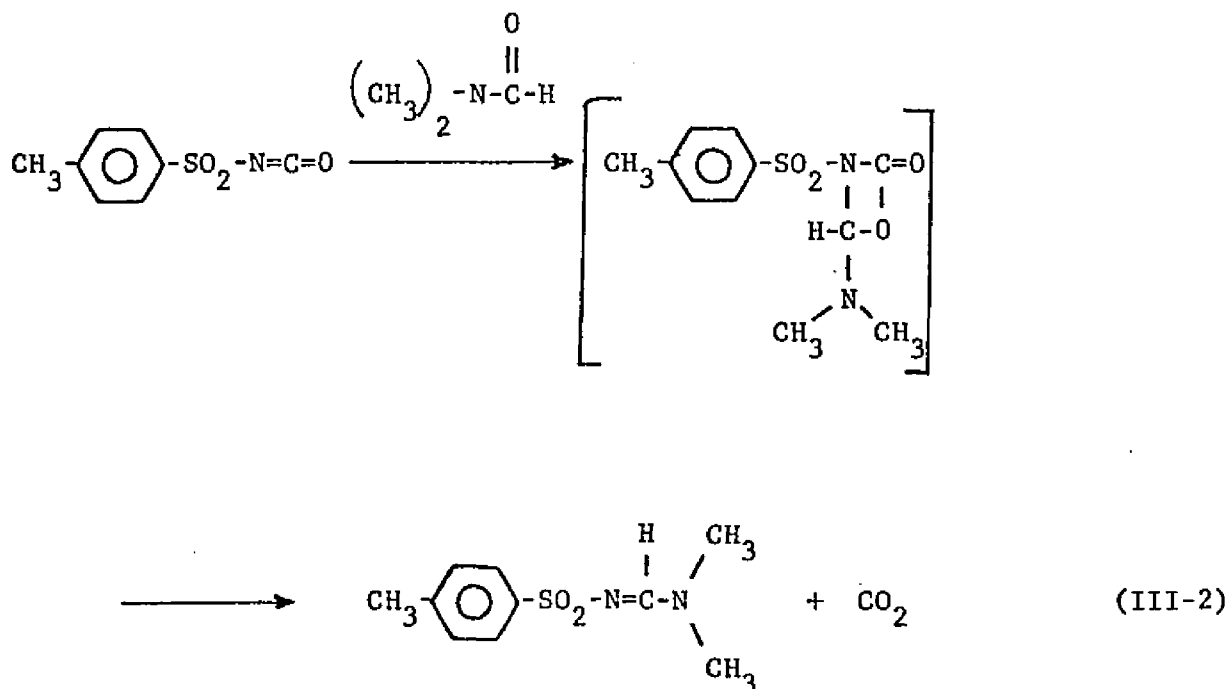
Since no work had previously been done on this derivative, a program was designed to completely investigate the reaction between para-toluenesulfonyl isocyanate and cellulose. Those factors which were investigated include the reaction media required, the effect of temperature on the reaction, the reaction rate, the effect of the initial reactant ratio, and the effect of catalysts. In these experiments the degree of substitution on the cellulose substrate was determined by the methods described in Chapter II; the precise method will be cited where appropriate.

### Reaction Media

Due to the reactivity of sulfonyl isocyanates the choice among various possible reaction media is limited. The polar aprotic solvents, i.e. dimethyl formamide and dimethyl sulfoxide, could not be used because they react with p-toluenesulfonyl isocyanate to produce N, N-dimethyl-N-p-toluenesulfonyl amidine and N-p-toluenesulfonyl dimethyl sulfilimine as shown in Equations (III-1) and (III-2). Other less polar







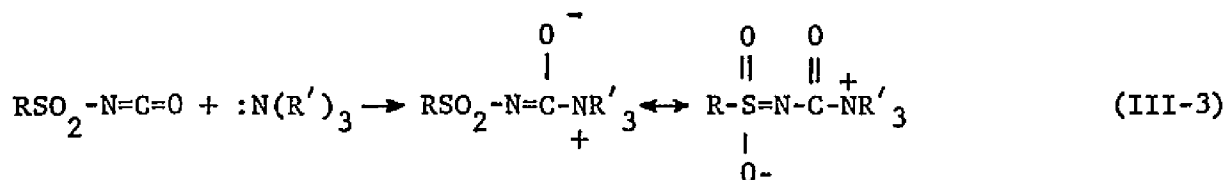
and less reactive solvents were tried as reaction media. Among these were chlorobenzene, xylene, dioxane, benzene, and *p*-toluenesulfonyl isocyanate. Analysis of the cellulose recovered showed that no substitution on the polymer chains had occurred in any of these media. In fact, a slurry of cotton linters in *p*-toluenesulfonyl isocyanate did not effect substitution after treatment at 80°C for 18 hours. The only effective system found for carrying out this reaction was that using pyridine as a reaction medium. Upon treating a slurry of cellulose fibers in pyridine with *p*-toluenesulfonyl isocyanate a clear viscous solution of the sulfonyl carbamate derivative is formed. Clearly, in order for the reaction to proceed it was necessary either for a tertiary amine to be present or for the reaction medium to dissolve the cellulose derivative. Two more reaction media were tried to ascertain which of these factors actually was required. A 60 percent benzene-40 percent pyridine mixture was used as one medium while the other was

triethylamine. If the mere presence of pyridine catalyzed the reaction, the benzene-pyridine mixture should be a good reaction medium. If it is the basicity of pyridine activating the reaction, then triethyl amine, a stronger base, should further enhance the reaction rate. This also assumes that the complex between triethyl amine and *p*-toluene-sulfonyl isocyanate is dissociated under the conditions employed (vide infra). No reaction occurred in either of these solvents indicating that the primary requirement for a reaction medium is the ability to dissolve the sulfonyl carbamate derivative.

The effect of the amount of pyridine required for reaction was qualitatively determined. It was learned that as little as 4 milliliters of pyridine per gram of cellulose is sufficient to promote the reaction. At the lower pyridine to cellulose ratios special techniques for adding the pyridine and the *p*-toluenesulfonyl isocyanate would be required to obtain a uniformly reacted product. A clear solution is obtained at concentrations as high as 10 weight percent cellulose but problems were encountered in the purification of the extremely viscous solutions produced by those systems having lower amounts of pyridine. However, it appears from weight gain of the cellulose that degree of substitution is not effected by the amount of pyridine used as long as the fibers are immersed.

#### Temperature Effects

Tertiary amines are normally considered to be catalysts for isocyanate reactions with alcohols as was shown in Chapter I. However, sulfonyl isocyanates form complexes with tertiary amines, as shown in Equation (III-3), reducing the reactivity of the isocyanate. Fortunately,



the complex formed is still reactive toward alcohols. When pyridine is the tertiary amine, the complex it forms with *p*-toluenesulfonyl isocyanate exhibits a very low pyridine solubility and a precipitate is observed when *p*-toluenesulfonyl isocyanate is added to a pyridine slurry of cellulose. Thus the concentration of active species in solution is very low at reaction temperatures below the melting point of the complex. The complex appears to melt between 75 and 80°C and there is a corresponding increase in the rate of substitution in this temperature range. Figure III-1 illustrates how the degree of substitution attained upon treating cellulose with a four to one ratio of *p*-toluenesulfonyl isocyanate to cellulose for one hour varies with temperature. This figure illustrates the rate enhancement caused by dissolution of the molten *p*-toluenesulfonyl isocyanate complex between 75° and 80°C.

### Catalysts

The effect of catalysts other than tertiary amines was also examined. The zinc chloride:pyridine complex used in promoting the reaction of phenyl isocyanate with cellulose was tried. After the reaction mixture of cotton linters, pyridine, and zinc chloride had been prepared, the *p*-toluenesulfonyl isocyanate was added. Immediately upon this addition the mixture turned a bright yellow color. The yellow color faded as the reaction proceeded. This suggests that another reaction intermediate was formed, further inhibiting reaction. A further disadvantage to using zinc chloride is that it is almost impossible to

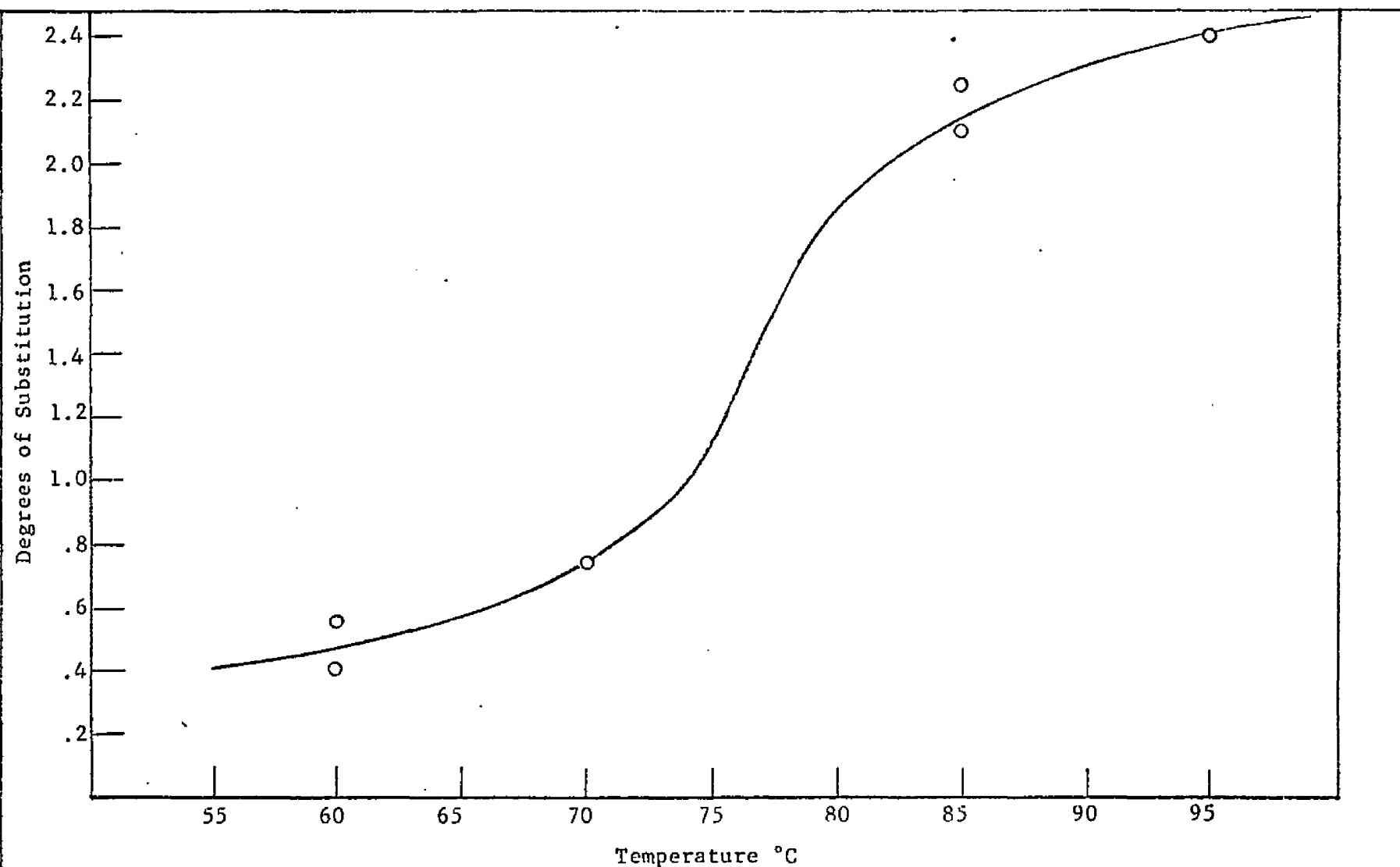


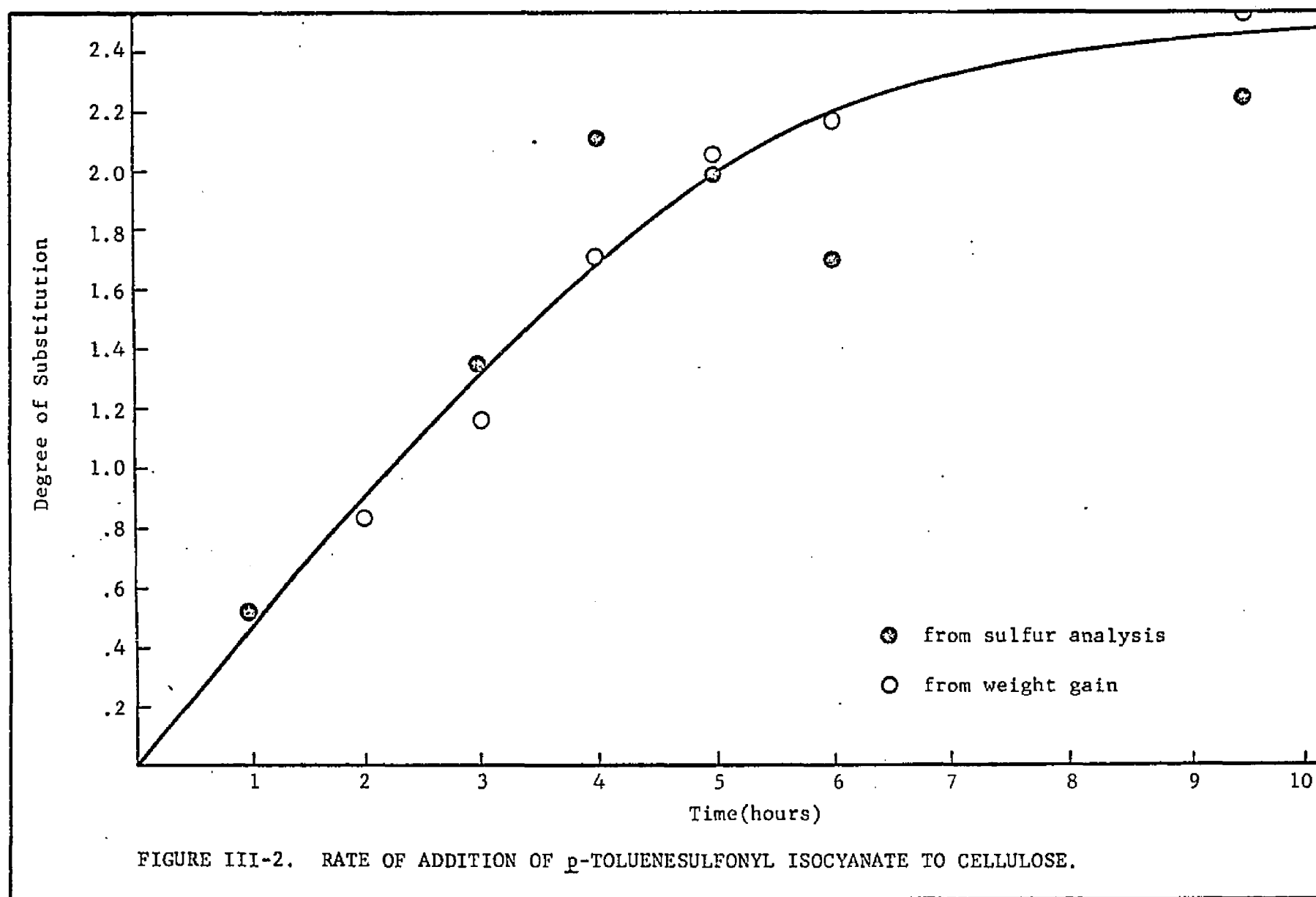
FIGURE III-1. DEGREE OF SUBSTITUTION vs REACTION TEMPERATURE.

to obtain and store in the anhydrous form. Dibutyl tin dilaurate was also tried as a catalyst but no increase in the rate of reaction was observed.

#### Reaction Rate

At 70°C the *p*-toluenesulfonyl isocyanate addition proceeds at a rate which could be easily followed by isolating and analyzing the cellulose derivative. The results, shown in Figure III-2, indicate a linear increase in the degree of substitution until a level of 2 is approached. Since there is no break in the curve at a degree of substitution of 1, it is reasonable to assume that there is little difference in the reactivity of sulfonyl isocyanates toward the primary and secondary alcohol functional groups on the cellulose chain. However, there is a decrease in the rate of addition around a degree of substitution of 2; this is probably due to strong steric hindrance to the addition of a third large pendulent group or to the electronic repulsion which would result if two sulfonyl carbamate anions were attached to adjacent carbon atoms.

It should be emphasized at this point, however, that the data shown in Figure III-2 actually represents several rate processes. In particular, they represent the process of diffusion of the *p*-toluenesulfonyl isocyanate through the fiber structure of the cotton linters to the reactant sites, the reaction itself, and the rate of solution of the polymer as it reacts. To complicate matters further each of these processes is dependent on the others and all vary as the reaction proceeds. Thus interpreting any information about the actual reaction kinetics from these data would not be on a sound basis. Should a kinetic model be desired one could be obtained by carrying out the



reaction on a cellulose derivative soluble in pyridine or in some other solvent which does not react with sulfonyl isocyanates. However, such a model would add further complications due to both additional steric factors and to electrical charges of other substituents on the cellulose molecule. For these reasons, this approach was not used in this research.

#### Initial Mole Ratio

The effect of the initial mole ratio of *p*-toluenesulfonyl isocyanate to cellulose was examined at 80°C. After 30 minutes reaction time, mixtures containing 1:1, 2:1, 3:1, and 4:1 moles of *p*-toluenesulfonyl isocyanate:cellulose were not visibly swollen, while those containing a ratio of 5:1 and above were progressively more swollen as the ratio of sulfonyl isocyanate increased. After one hour 3:1 and 4:1 mixtures were swollen while those above 6:1 were beginning to dissolve. Swelling of the 2:1 system had occurred after 3 hours. An increase in solubility was obvious as the ratio of the sulfonyl isocyanate to cellulose was increased. A total reaction time of eighteen hours resulted in swelling for the 1:1 system and while systems having ratios of up to 3:1 still had a large portion of fibrous material, those at 4:1 and above were almost completely fiber free.

#### Mixed Derivatives

The results of the study on the reaction of *p*-toluenesulfonyl isocyanate with cellulose show that this reaction proceeds using untreated, highly crystalline cellulose without the need of the application of swelling agents. Further, the reaction can be controlled so that a uniform derivative which is swollen in pyridine can be produced

at a low degree of substitution. This system may then be used for other reactants with cellulose to produce a variety of mixed derivatives. Such mixed derivatives were prepared with monochloroacetic acid, acetic anhydride, and a variety of aryl isocyanates.



### C. Characterization of Cellulose Derivatives

#### Infrared Spectra

Infrared characterization of polymer systems can be useful in several ways. Its use in this research was mainly in determining whether or not a chemical modification of cellulose had occurred and also in giving information as to the kind of modification; i.e., what are the pendulent groups and how are they attached to the substrate? Infrared spectra were obtained for a potassium bromide pellet of pure cellulose (Figure III-3). Cellulose was found to have a diffuse spectra with only a few broad absorptions rather than any well defined sharp peaks. However, no significant absorptions were observed in the carbonyl region ( $1750\text{--}1700\text{ cm}^{-1}$ ) or below  $900\text{ cm}^{-1}$  where strong phenyl absorptions would be anticipated. The cellulose derivatives prepared in this work all exhibited strong absorptions in these regions; this was considered positive evidence for the formation of carbamate linkages.

The spectrum of a potassium bromide pellet of cellulose phenyl carbamate is shown in Figure III-4. Radical changes in the cellulose spectra can be observed. Structural assignments to these peaks are given in Table III-1. The strong absorption peaks at  $740$  and  $680\text{ cm}^{-1}$  as well as weaker absorptions at  $1640$ ,  $1165$ ,  $1150$  and  $1050\text{ cm}^{-1}$  are consistent with the presence of the monosubstituted benzene group. The strong peak at  $1700\text{ cm}^{-1}$  has been assigned to the carbonyl group in the urethane (carbamate) structure. Other evidence of the linkage structure are the peaks at  $1530\text{ cm}^{-1}$  for secondary amide and  $1205\text{ cm}^{-1}$  for the C-O ester structure (1).

Similar information was obtained from spectra of cellulose

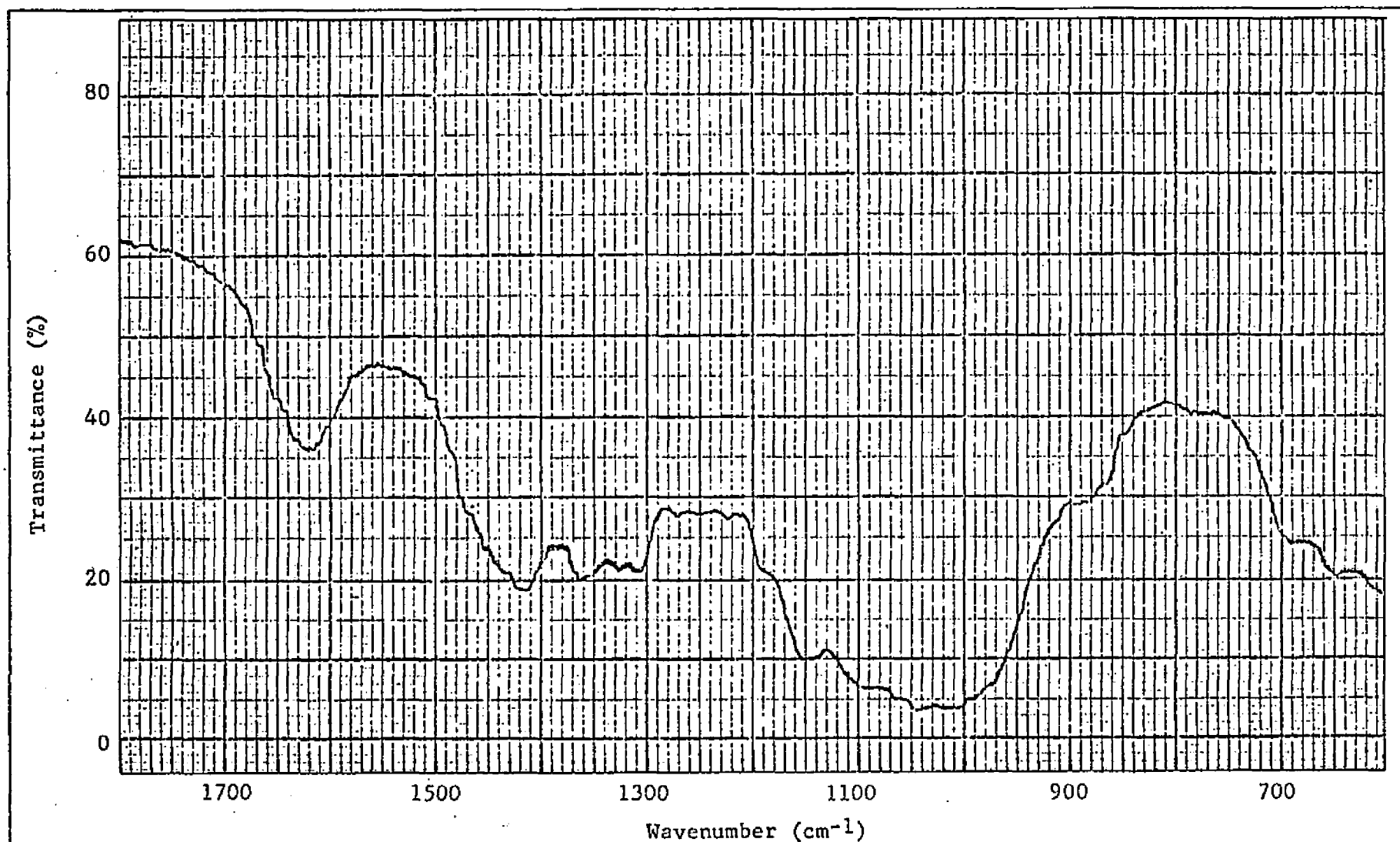


FIGURE III-3. IR SPECTRA OF KBr PELLET OF COTTON LINTERS.

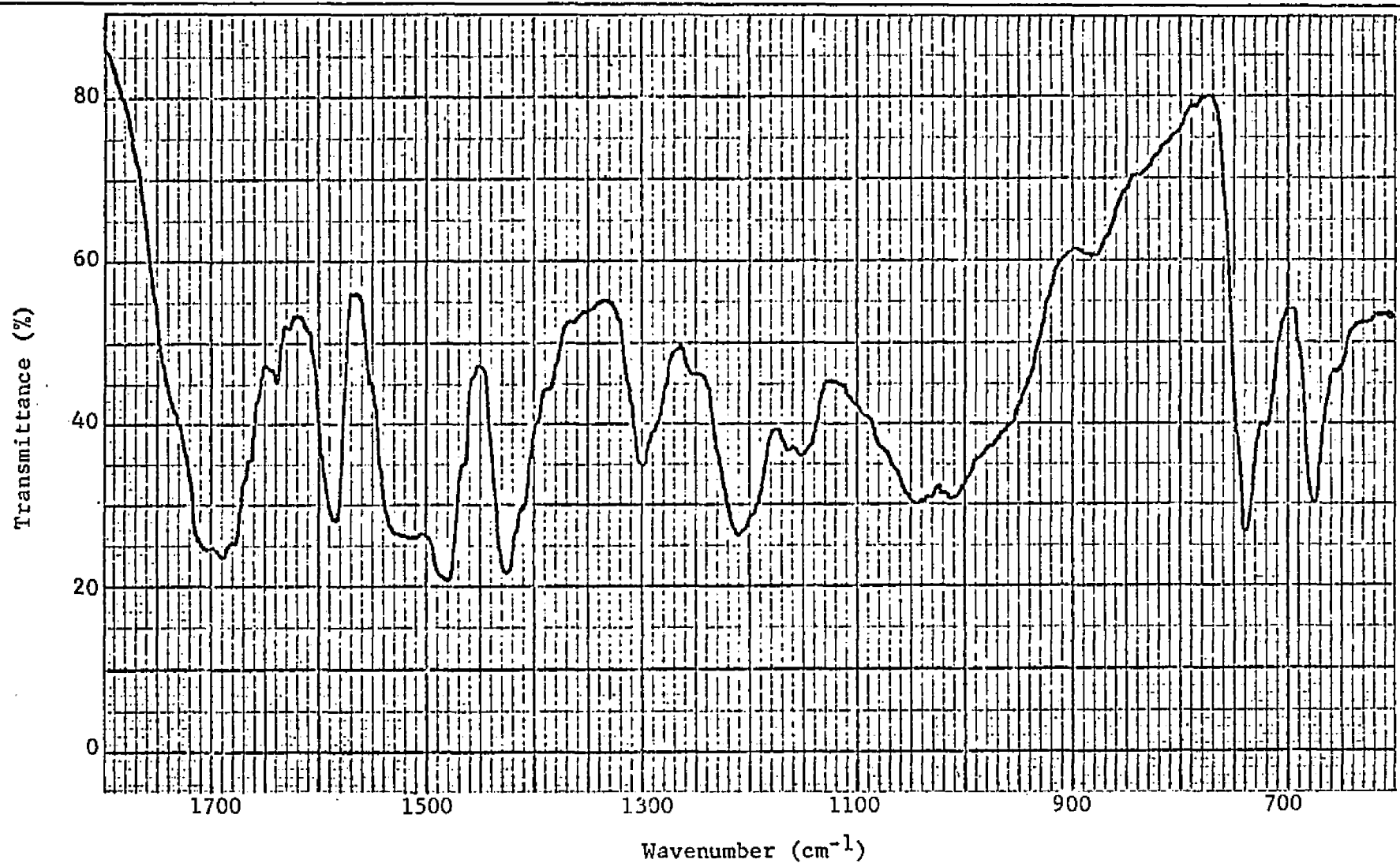


FIGURE III-4. IR SPECTRA OF KBr PELLET OF CELLULOSE PHENYL CARBAMATE.

TABLE III-1

## CELLULOSE PHENYL CARBAMATE SPECTRA (1)

<u>Peak (cm<sup>-1</sup>)</u>	<u>Assignment</u>
1700	carbonyl
1640	phenyl
1590	phenyl, NH
1530	secondary amide
1480	phenyl, OH
1430	-OH
1300	-OH
1205	C-O (ester)
1165	phenyl
1150	phenyl
1050	phenyl, OH
740	phenyl
680	phenyl

p-toluenesulfonyl carbamate shown in Figures III-5 and III-6. Complete assignments have been made for this derivative in Table III-2. These spectra exhibit some significant differences from the spectrum of the phenyl carbamate derivative which are mainly due to the introduction of the sulfonyl group into the carbamate structure and the addition of a methyl group onto the phenyl ring to give a p-tolyl derivative. These changes are illustrated by sulfonyl (sulfone) peaks at 1325 and 1150  $\text{cm}^{-1}$  and methyl peak at 1400  $\text{cm}^{-1}$  along with numerous disubstituted benzene peaks. Peak assignments at 910, 800, 740, 690, 670, and 650  $\text{cm}^{-1}$  were made on the basis of spectra containing the groups shown in Table III-2 (2, 3). Figures III-5 and III-6 also illustrate the poorer resolution obtained from the solid RBr pellet as compared to that of a film spectra. Unfortunately, some uncertainty exists in the film spectra because of possible contamination by unremoved solvent.

A spectrum of a mixed derivative formed by reacting phenyl isocyanate and p-toluenesulfonyl isocyanate with cellulose is shown in Figure III-7. Note that peaks which are common to both the carbamate and sulfonyl carbamate linkages are sharper and have a stronger absorbance than those which are unique to one of the structures. Examples of this are the sharpness of the N-H peak at 1590  $\text{cm}^{-1}$ , the secondary amide peak at 1525  $\text{cm}^{-1}$  and the C-O ester peak at 1210  $\text{cm}^{-1}$  as well as the broadening of the carbonyl peak at 1700  $\text{cm}^{-1}$ . Also observe the relative weakness of the peaks between 800 and 900  $\text{cm}^{-1}$  as compared to those of the pure sulfonyl carbamate derivative.

#### Solubility Properties

Because some polymers do not exhibit softening or melting temperatures, and thus cannot be fabricated by melt techniques, the solubility

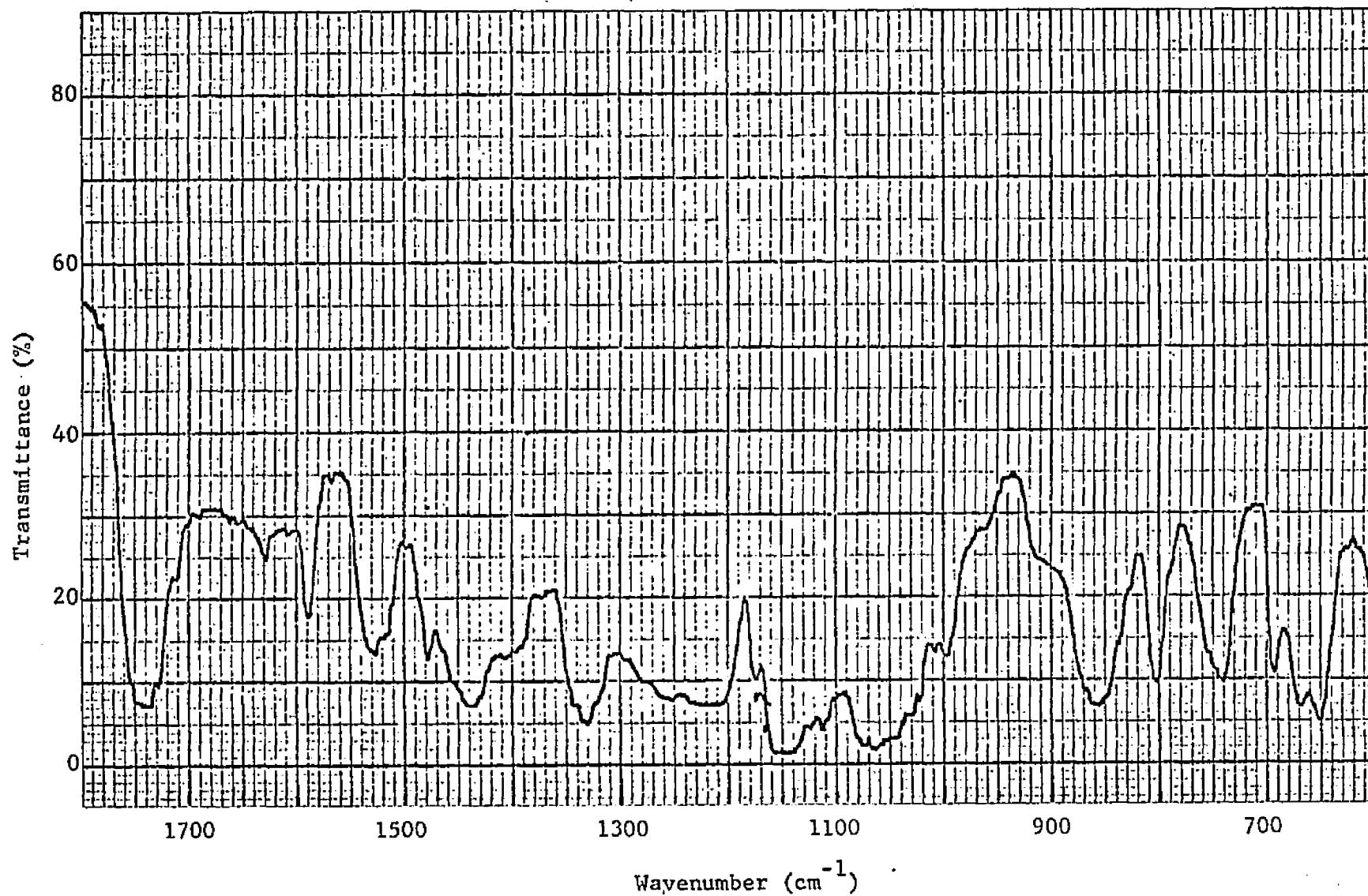


FIGURE III-5. IR SPECTRA OF KBr PELLET OF CELLULOSE *p*-TOLUENESULFONYL CARBAMATE.

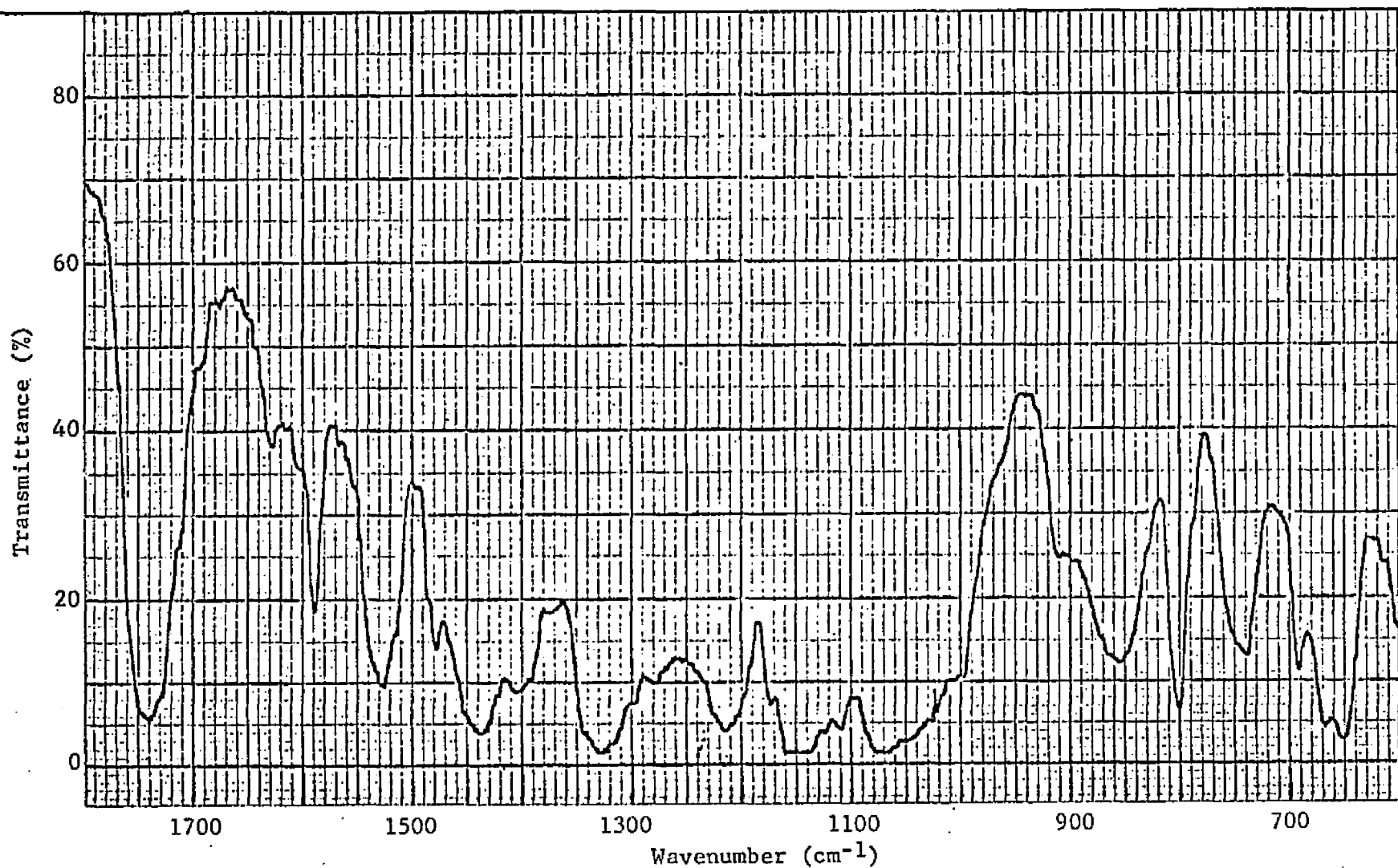
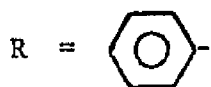


FIGURE III-6. IR SPECTRA OF CELLULOSE *p*-TOLUENESULFONYL CARBAMATE FILM.

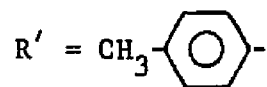
TABLE III-2

CELLULOSE P-TOLUENESULFONYL CARBAMATE (1)

<u>Peak (cm<sup>-1</sup>)</u>	<u>Assignment</u>	<u>Peak (cm<sup>-1</sup>)</u>	<u>Assignment</u>	<u>Peak (cm<sup>-1</sup>)</u>	<u>Assignment</u>
1740	carbonyl	1325	-SO <sub>2</sub> -	910	R-SO <sub>2</sub> -NH-CO <sub>2</sub> - <sup>a</sup>
1630	p-tolyl	1280	-OH	855	p-tolyl
1590	N-H	1215	C-O (ester)	800	R'-SO <sub>2</sub> - <sup>b</sup>
1525	p-tolyl, secondary amide	1175	p-tolyl	740	R-SO <sub>2</sub> -NH-CO <sub>2</sub> - <sup>a</sup>
1480	CH <sub>3</sub> -C, OH	1150	-SO <sub>2</sub> -	690	R'-SO <sub>2</sub> - <sup>b</sup>
1440	-OH	1110	p-tolyl	670	R-SO <sub>2</sub> -NH-CO <sub>2</sub> - <sup>a</sup>
1400	CH <sub>3</sub> -C	1060	p-tolyl, -OH	650	R'-SO <sub>2</sub> - <sup>b</sup>



a reference 2



b reference 3



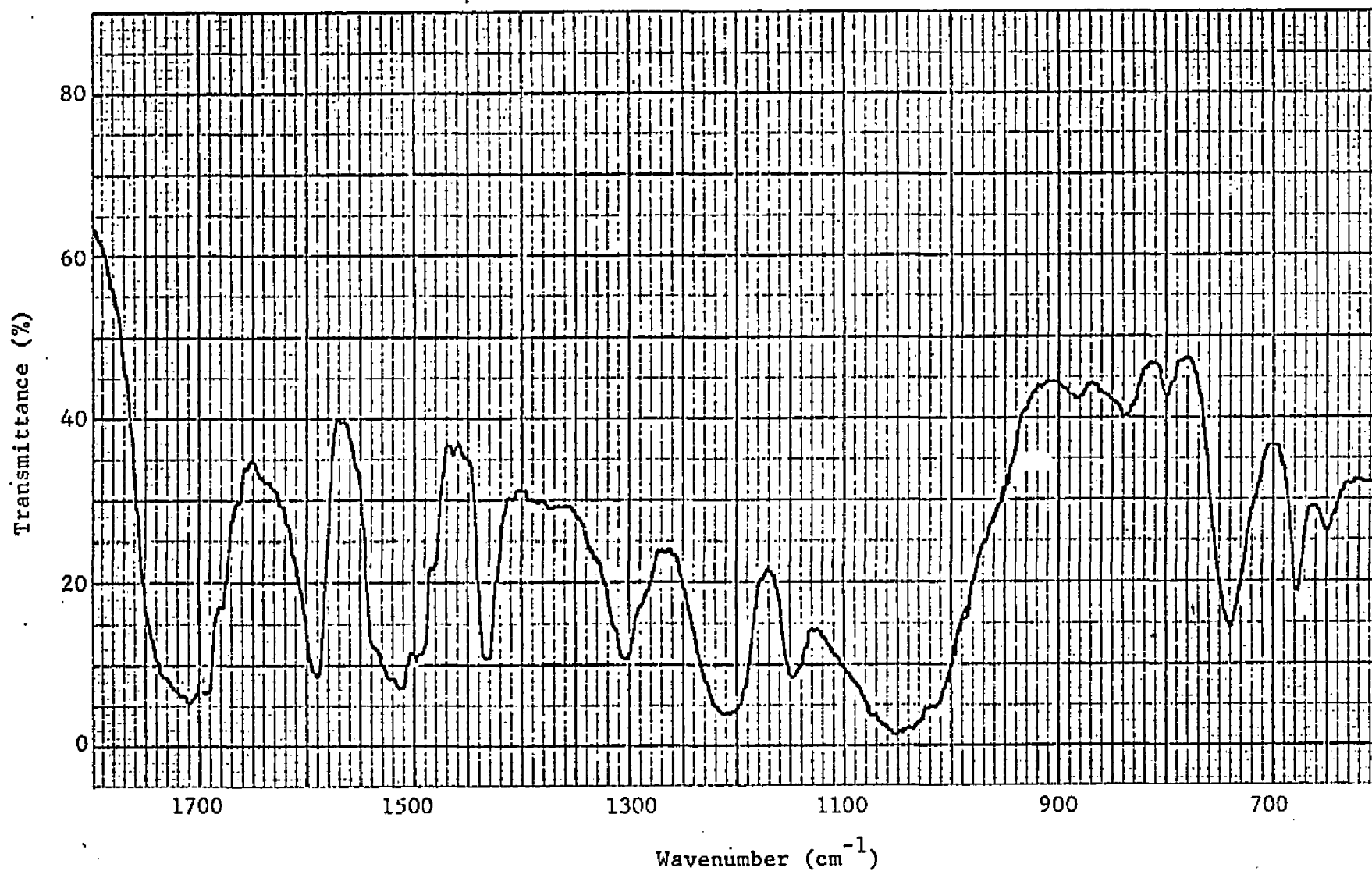


FIGURE III-7. IR SPECTRA OF KBr PELLET OF MIXED CELLULOSE CARBAMATES.

characteristics of a new polymer often determine its range of application. Solubility properties of cellulose *p*-toluenesulfonyl carbamate have been determined in various concentrations of sodium hydroxide as well as in several common organic solvents. The results of the solubility studies in alkaline solutions are given in Table III-3 while those for organic solvents are in Table III-4.

The solubility data shown in these tables represent some of the most unusual information obtained in this research. As shown in Table III-3, the solubility of this cellulose derivative was greater in dilute sodium hydroxide (2%) than in the more concentrated solutions (10%). Such a phenomena has not been previously reported for other cellulose derivatives. The insolubility at the higher caustic concentrations may be due to higher ionic strength, however solutions of the derivative in 2% caustic remained homogeneous when sodium chloride was added to bring the total concentration of salt and sodium hydroxide to ten percent. The fact that little order can be made of these data is startling. Cellulose derivatives usually go through one region of degrees of substitution which are soluble in a given type of solvent but the data show three regions of substitution in which this derivative has enough hydrophilic nature to become swollen in aqueous mixtures. A similar irregularity is noted in the columns for 5 and 10 percent caustic solutions. These characteristics may be due to the unusual nature of the sulfonyl carbamate substituent groups, which could cause hydrogen bonding in regions of substitution which permit solvation in specific solvent environments. Some slight variation in the history of the derivative could also effect the solubility characteristics but care was taken to treat all as nearly alike as possible. One advantage

TABLE III-3

ALKALI SOLUBILITY OF CELLULOSE *p*-TOLUENESULFONYL CARBAMATE

<u>D. S.</u>	<u>H<sub>2</sub>O</u>	<u>2% NaOH</u>	<u>5% NaOH</u>	<u>10% NaOH</u>
0	I	I	I	I
0.1	swollen	I	swollen	swollen
0.3	swollen	I	I	I
1.1	I	S	S	swollen
1.4	swollen	S	I	I
1.6	I	S	S	swollen
2.3	swollen	S	I	I

TABLE III-4

## SOLVENTS FOR CELLULOSE p-TOLUENESULFONYL CARBAMATE

Solvent	D. S.	0	0.1	0.3	0.7	1.1	1.4	1.6	2.0	2.3	2.8
Acetone		I	I	I	I	I	swollen	I	I	I	swollen
Chloroform		I	I	I	I	I	I	I	I	I	--
Dimethylformamide		I	I	swollen	swollen	S	S	S	swollen	S	swollen
Dimethylsufoxide		I	I	swollen	swollen	S	S	S	swollen	S	swollen
Dioxane		I	I	I	I	swollen	I	I	I	I	--
Ethanol		I	I	I	I	I	I	I	I	I	I
Hexane		I	I	I	I	I	I	--	I	I	--
33% Methanol - 67% Benzene		I	--	--	--	--	I	I	--	--	--
Pyridine		I	I	swollen	S	S	S	S	S	S	swollen
Tetramethyl ammonium hydroxide		I	--	--	--	S	--	--	--	--	--
Triethylamine		I	--	--	I	--	--	--	I	I	--
Ethanolamine		--	I	--	swollen	swollen	--	swollen	--	--	--

of these solubility characteristics is that an approximation of the degree of substitution can be obtained by simply checking the solubility in water, 2 percent NaOH, 5 percent NaOH, and 10 percent NaOH.

The organic solubility data of Table III-4 are more consistent with normal trends in polymer solubility data. Even so some of the data are irregular. For example, there are two regions of degrees of substitution in which the derivative is swollen in acetone and there is also some irregularity in the solubility data of dimethyl formamide and dimethyl sulfoxide. These data indicate that cellulose *p*-toluene-sulfonyl carbamate has regions of solubility in polar aprotic solvents and in pyridine. It is interesting to note that even though the derivative is soluble in pyridine it is not soluble in a stronger base, triethyl amine. The polymer probably forms an ammonium salt with all amines but fails to dissolve because the excess amine does not solvate the salt. When the amine group is coupled with a hydrophilic hydroxyl group, i.e. ethanolamine, dissolution occurs.

It was also observed that at concentrations as low as one percent a pyridine solution of the sulfonyl carbamate derivative formed a thick gel at temperatures below twenty-seven to twenty-eight degree Centigrade. The gel could be broken by raising its temperature above this level, indicating that gellation had not been caused by the formation of primary intermolecular bonds between polymer molecules. The process could be repeated ad infinitum with no change in either the solution above 28°C or the gel below 28°C.

When a hot (above 28°C) pyridine solution of the derivative was stirred in an open vessel, then sealed, not only did a gel form after cooling, but the gel began collapsing in on itself ejecting the

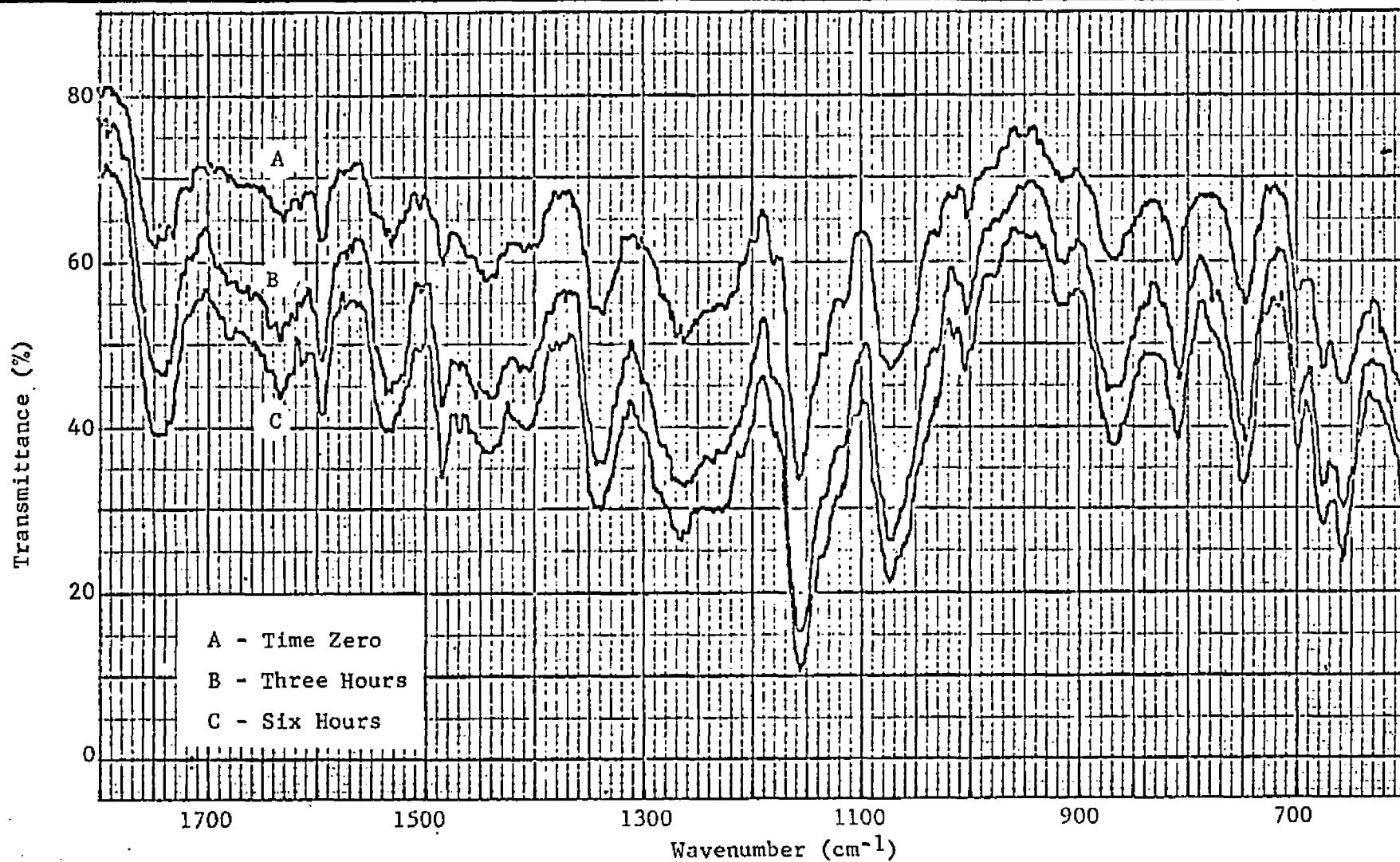


FIGURE III-8. SPECTRA OF PYRIDINE SMEAR OF CELLULOSE *p*-TOLUENESULFONYL CARBAMATE.

pyridine. This process is extremely slow but most remarkable in that the shrinkage is completely uniform and will retain the shape of the interior of its container. This is true even though the gel might shrink to a very small fraction of its initial size.

A smear of the thick viscous solution was made on a sodium chloride crystal. Infrared spectra of the gel were run at three intervals and are shown in Figure III-8. No evidence of a change in the chemical structure of the gel could be detected. Because solvent is evaporating all the time these spectra were being run, stronger and sharper peaks are observed with spectrum C as compared to A.

#### Thermal Properties

The thermal properties are just as important as solubility in determining possible applications of a new polymer. Important properties such as melt temperature and glass transition temperature certainly affect not only how a polymer can be used but also its method of manufacture. There are a few cellulose derivatives which have glass transitions and melt points, but those investigated in this research did not. Thermal stability is also important. Here the pertinent questions are what temperature does degradation begin, to what extent does it occur and what are the decomposition products formed? These questions have been answered for the thermal degradation of sulfonyl carbamates.

Thermal degradation of cellulose derivatives can occur in three possible ways. The cellulose chain can depolymerize; the anhydroglucose ring can be opened; or the bond holding the pendant group to the substrate can rupture. To investigate how degradation occurs in carbamates and sulfonyl carbamates differential thermograms were obtained for purified cotton linters (Figure III-9), cellulose phenyl carbamate (Figure

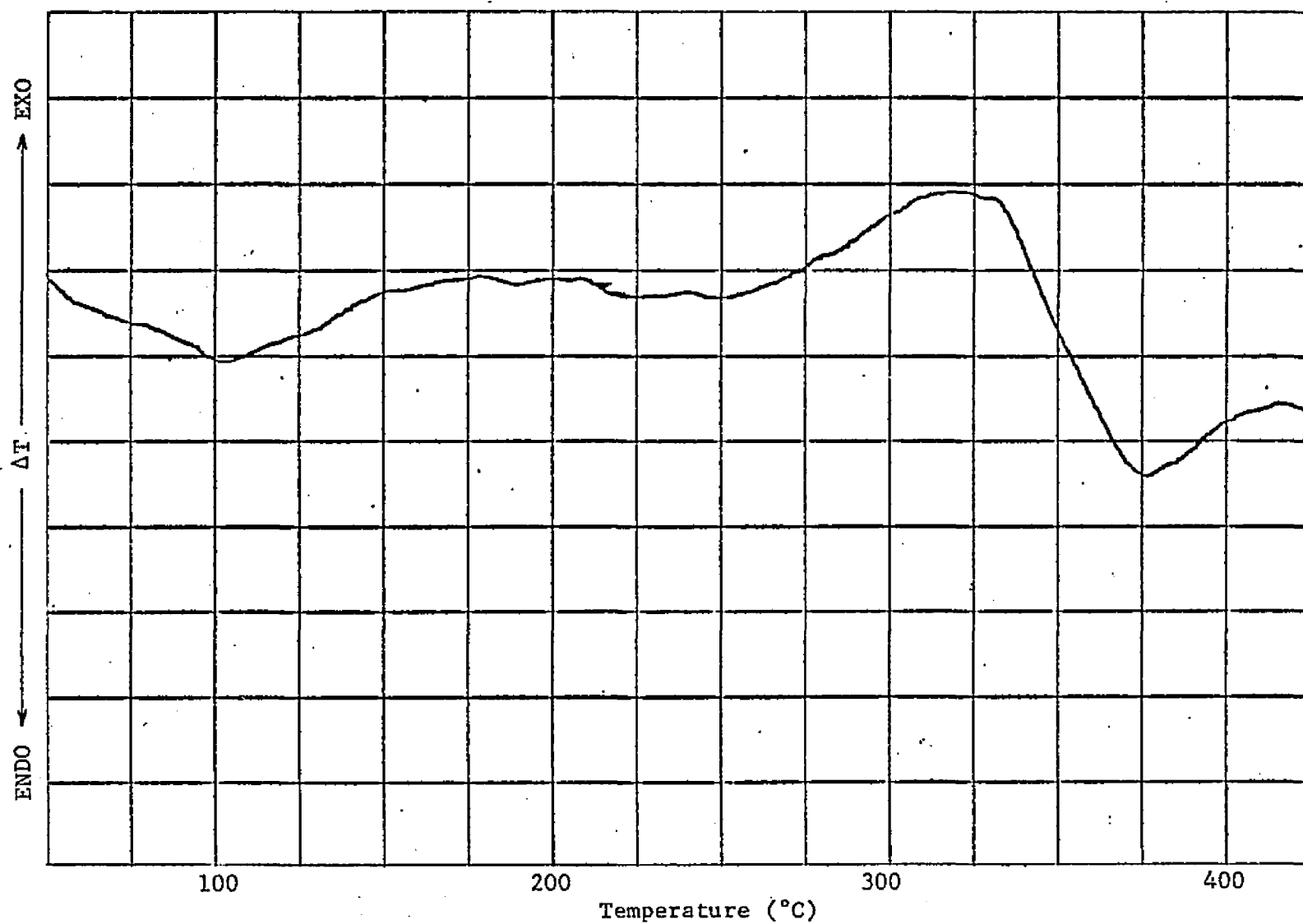


FIGURE III-9. DTA THERMOGRAM OF PURE COTTON LINTERS.



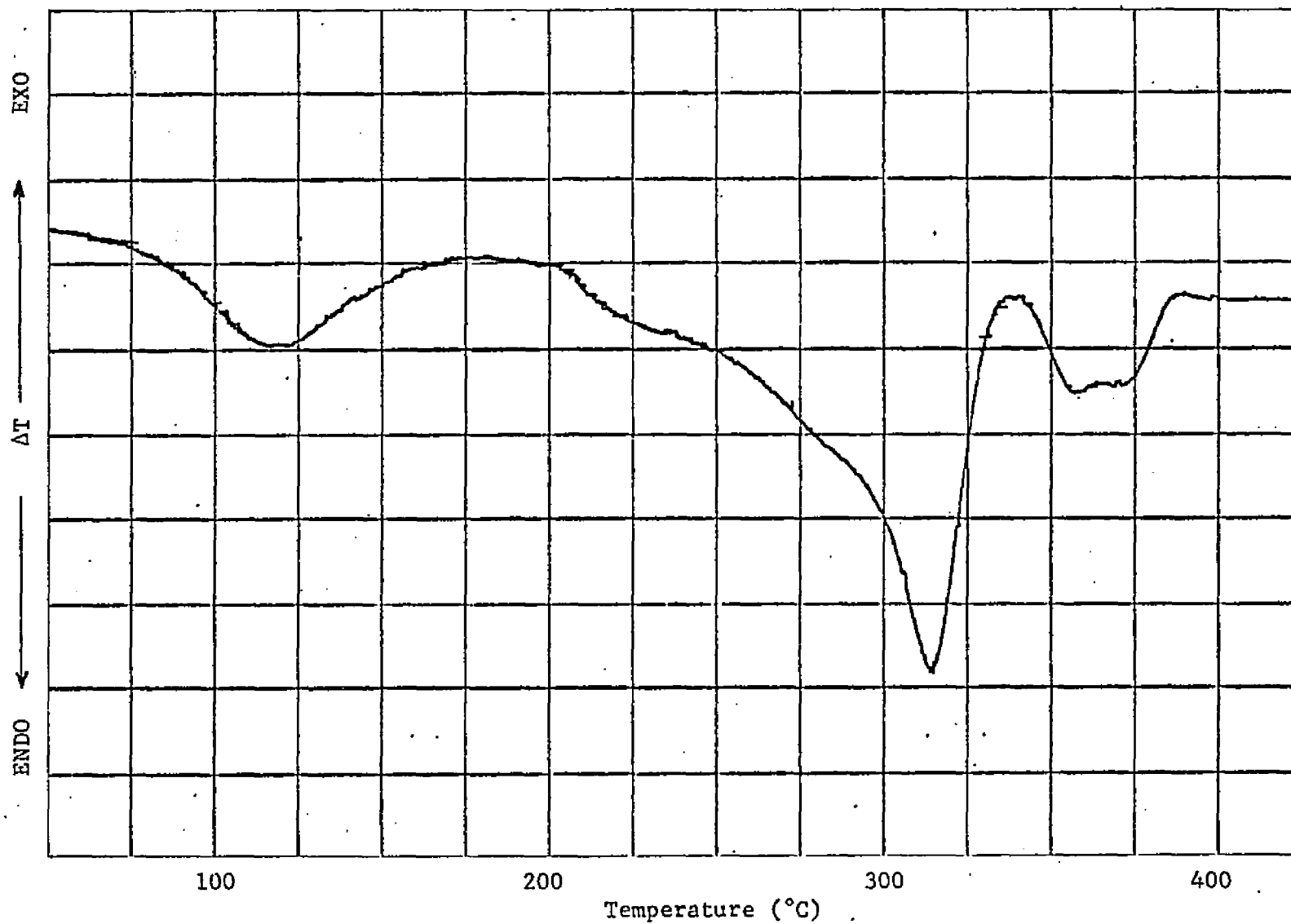


FIGURE III-10. DTA THERMOGRAM OF CELLULOSE PHENYL CARBAMATE.

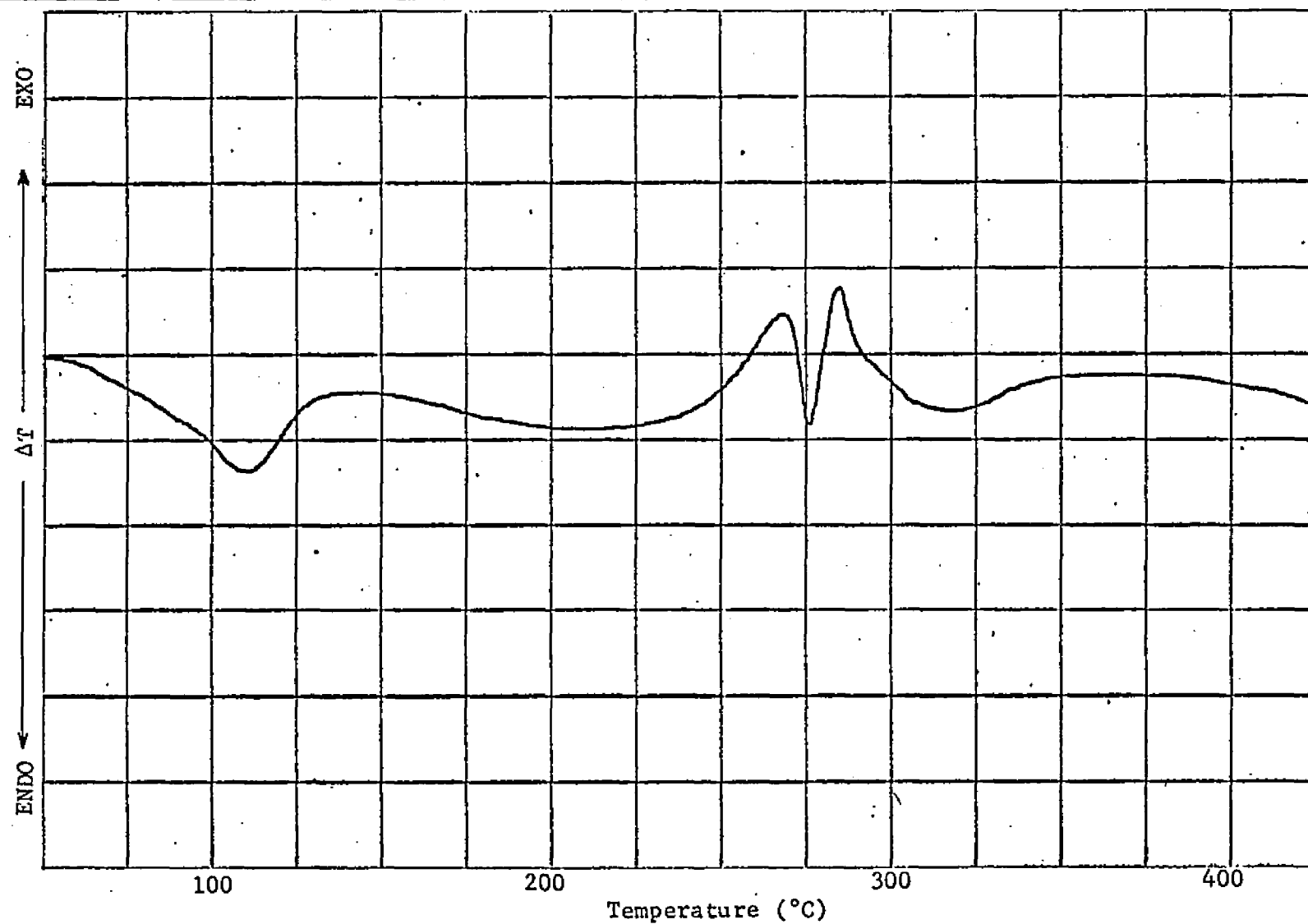
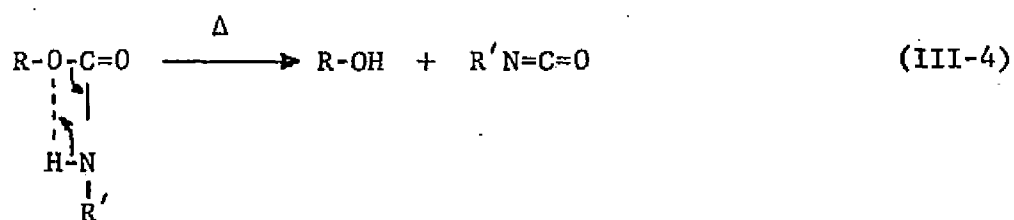


FIGURE III-11: DTA THERMOGRAM OF CELLULOSE p-TOLUENESULFONYL CARBAMATE.

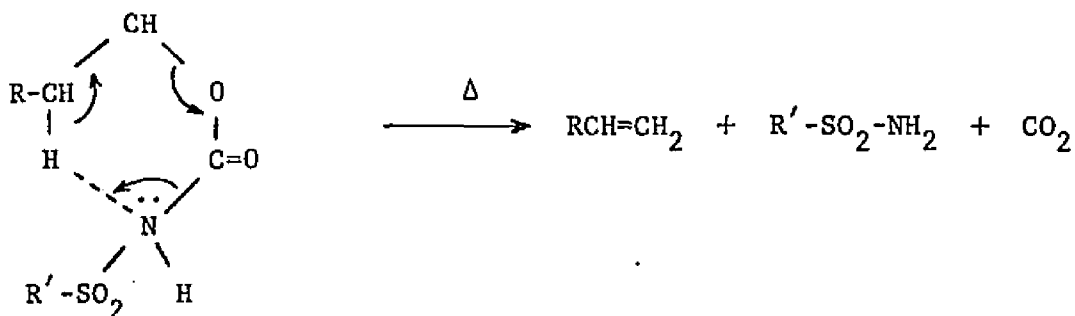
III-10), and cellulose *p*-toluenesulfonyl carbamate (Figure III-11). Analysis of these curves shows that all of them have endothermic peaks occurring around 100°C. These can be attributed to the removal of adsorbed moisture. The endothermic peak for pure cellulose occurring near 335°C indicates that it is at this temperature rapid degradation begins. Endothermic peaks are observed at about 300°C for the phenyl carbamate derivative and at about 250 to 275°C for the *p*-toluenesulfonyl carbamate derivative. These are attributed to ruptures of the carbamate linkages.

Mack and Hobart (4) investigated the decomposition temperatures of various carbamate derivatives of cellulose and report that the more electron withdrawing the substituent attached to cellulose by the carbamate linkage, the higher the temperature of cleavage. The data obtained for sulfonyl carbamates violate this principle. The same investigators reported that the rupture of the carbamate linkage was by a four-centered reaction mechanism as shown by Equation (III-4). This mechanism



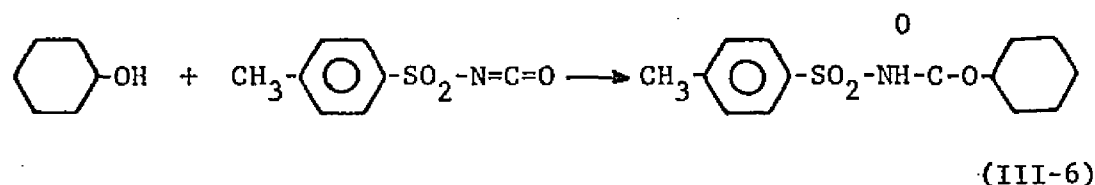
requires the evolution of the isocyanate and regeneration of the alcohol.

Since a temperature much lower than expected was observed for decomposition of sulfonyl carbamates it was postulated that a change in reaction mechanism must be involved with their degradation. A logical reaction mechanism is a six-centered one as is shown by Equation (III-5).



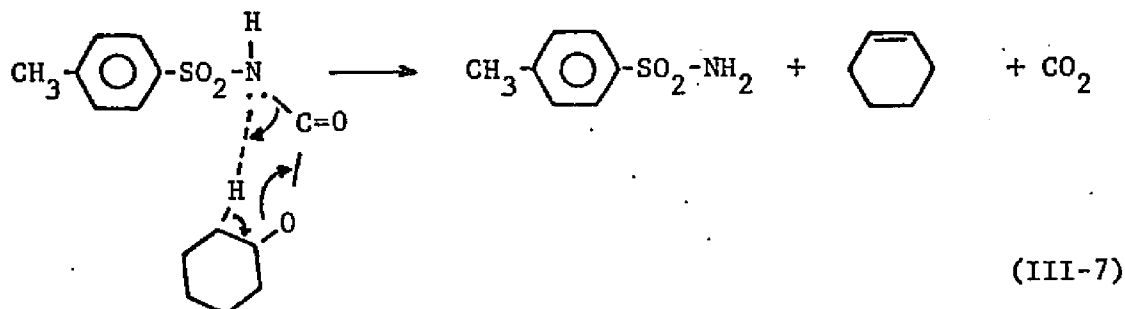
(III-5)

To obtain further evidence about sulfonyl carbamates decomposition a model compound was formed as in Equation (III-6). A differential



(III-6)

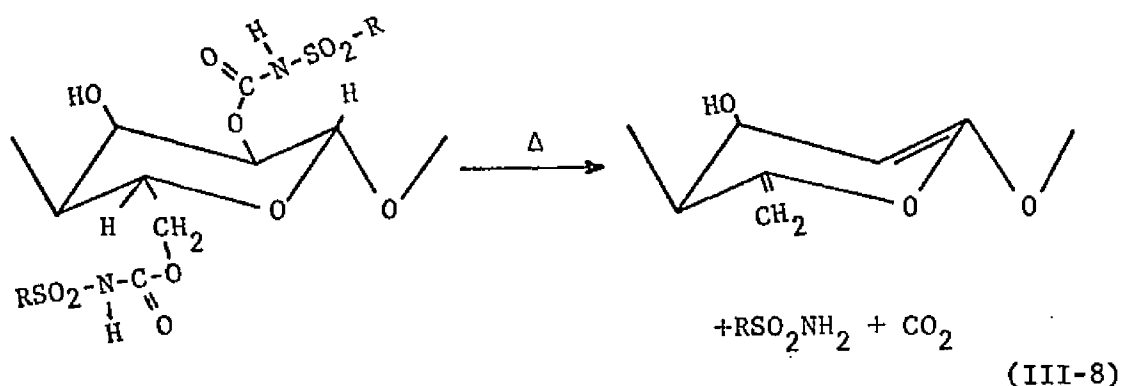
thermogram of the model compound was run (Figure III-12) and shows that the sulfonyl carbamate bond does rupture at about 250-260°C. A sample of the model was decomposed under controlled conditions and resulted in the isolation of *p*-toluenesulfonamide and a liquid having the characteristic infrared absorption peaks of cyclohexene. The recovered liquid decolorized bromine, thereby indicating an olefinic nature, and also had an odor similar to cyclohexene. As shown in Equation (III-7), this information fits the proposed reaction mechanism



(III-7)

of Equation (III-5).

A sample of cellulose *p*-toluenesulfonyl carbamate was thermally degraded under vacuum in the microsublimation apparatus discussed in Chapter II. Analysis of all the bands formed was impossible but the first bond formed was found to be *p*-toluenesulfonamide. This agrees with the postulated mechanism of decomposition. Equation (III-8) shows what this mechanism would look like for the cellulosic carbamate of D.S. 2.



It is well known that the sodium salt of carboxymethyl cellulose is more thermally stable than the acid form. Therefore a differential thermogram was run on the sodium salt of cellulose *p*-toluenesulfonyl carbamate. This salt was prepared by precipitating an alkali solution of the acid derivative in ethanol and was purified by washings in 75% ethanol - 25% water. The thermogram (Figure III-13) shows a decomposition peak 25 degrees above the acid form, thus indicating that the salt form is more stable than the acid.

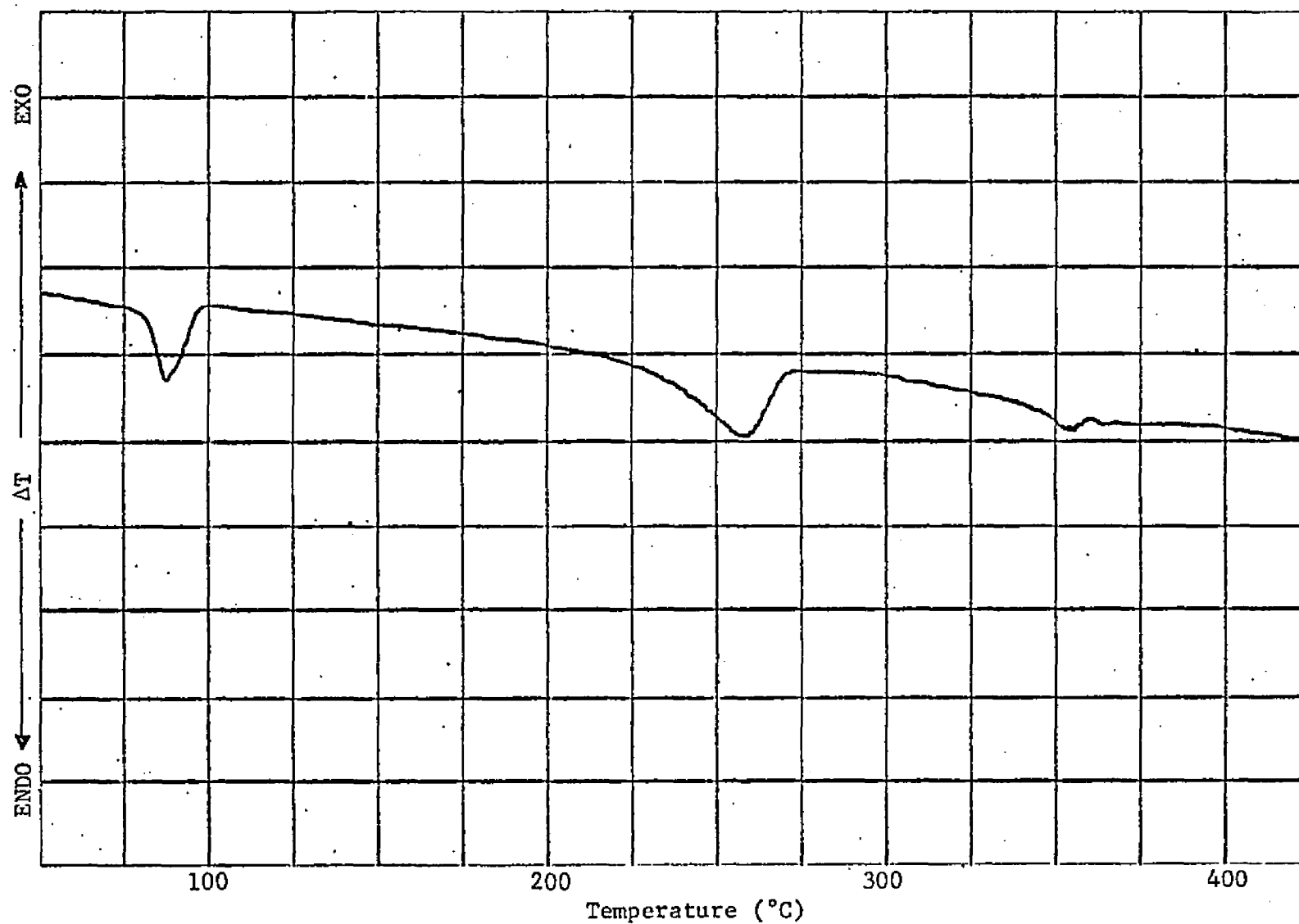


FIGURE III-12. DTA THERMOGRAM OF O-CYCLOHEXYL-N-p-TOLUENESULFONYL CARBAMATE.

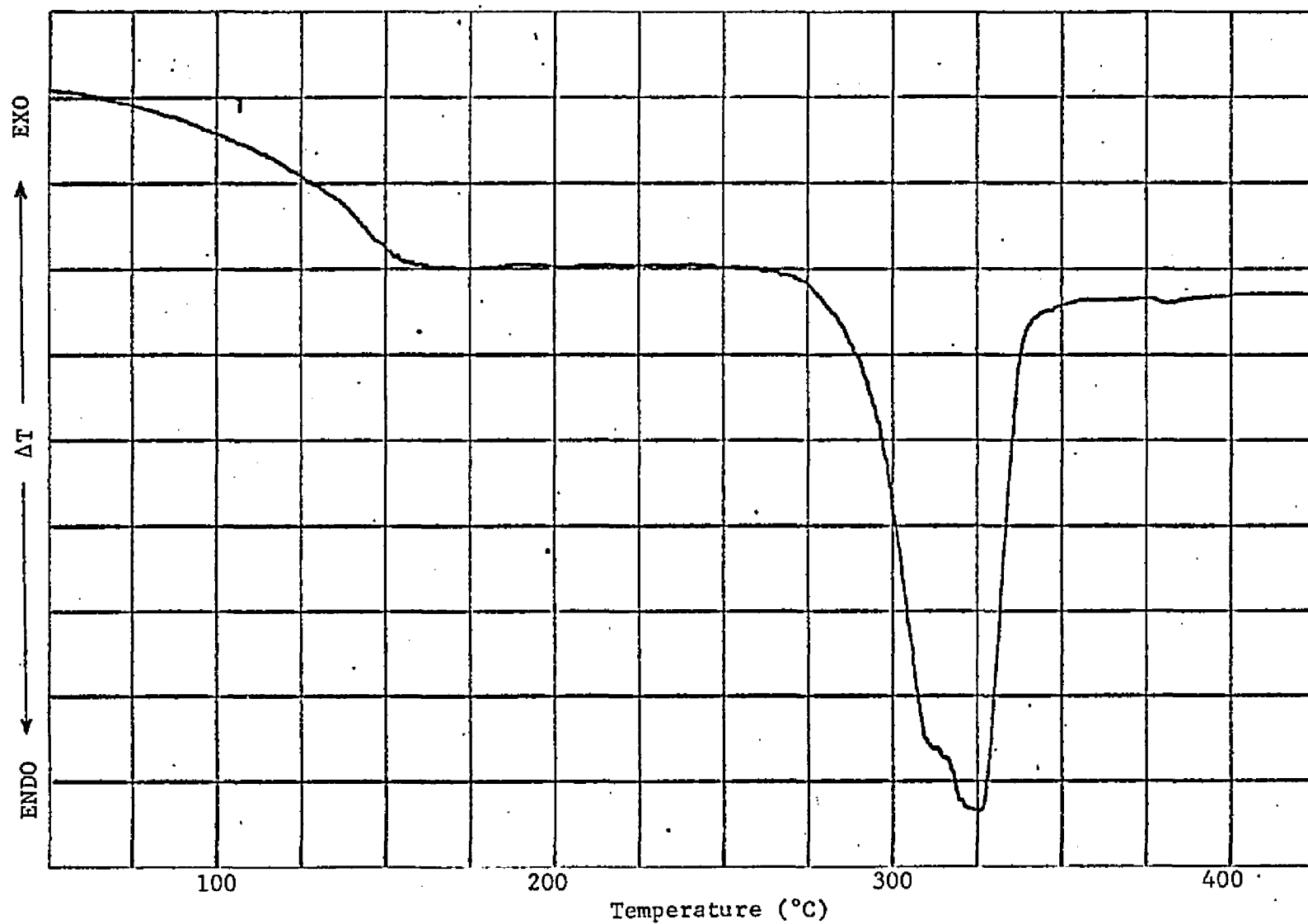


FIGURE III-13. DTA THERMOGRAM OF SODIUM SALT OF CELLULOSE *p*-TOLUENESULFONYL CARBAMATE.

#### D. Application Studies on Cellulose p-Toluenesulfonyl Carbamate

The initial purpose behind the investigation of cellulose sulfonyl carbamates was that it was believed they might be used as ion exchange resins. Most of this section is devoted to establishing their utility in this area. However, because these derivatives represent a new polymer, preliminary studies were also made on some other possible applications of these polymers.

##### Ion Exchange

Traditionally, there are two major areas studied in the evaluation of a new ion exchange resin. The first involves determining the actual ion exchanging characteristics of the resin while the second is aimed more at evaluating the physical properties that might effect the usefulness of the exchange resin. Some of the more important ion exchange characteristics which were evaluated include ion exchange capacity, the effect of crosslinking on ion exchange capacity, the effect of degree of substitution on ion exchange capacity, the ability of the resin to be regenerated and the type of functionality possessed by a given resin. Some of the physical properties effecting the usefulness of the resins are the physical nature of the resin (i.e. is it granular, fibrous, etc.), and the swelling of the resin by alkaline solutions.

A study of the ion exchange capabilities of cellulose p-toluenesulfonyl carbamates has shown that the hydrogen present on the carbamate nitrogen is acidic enough to serve as a site for cation exchange. Figure III-14 is the titration curve of this derivative with standard HCl solution. Comparison of this curve with the characteristic curves of weak and strong acid ion exchange resins of Figure I-7, indicates that this derivative falls in the weakly acidic group of ion exchangers.



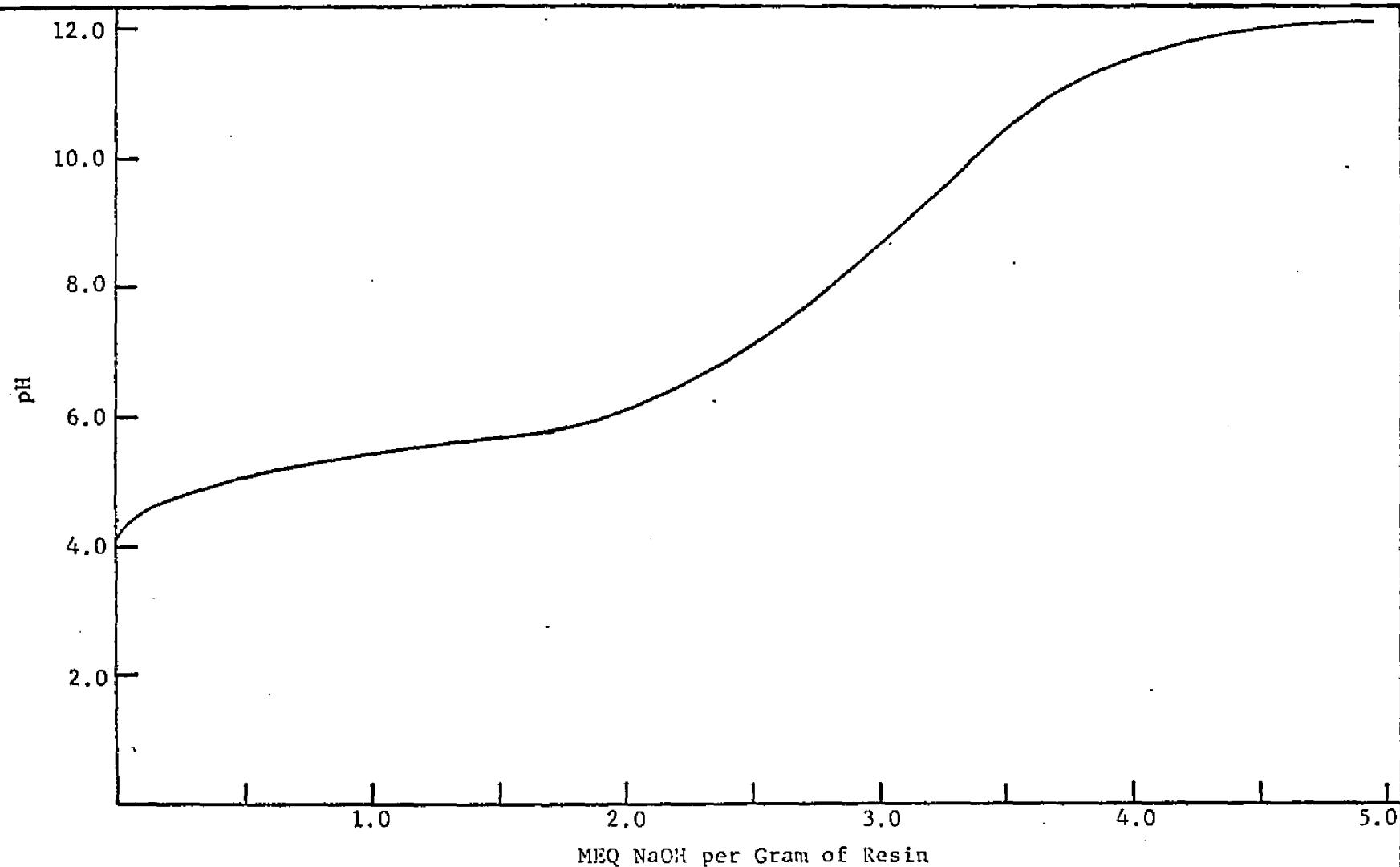


FIGURE III-14. TITRATION CURVE OF CELLULOSE p-TOLUENESULFONYL CARBAMATE.

This development introduces a new ionogenic group with potential cationic exchange capability to the field of ion exchange.

The ion exchange capacities of cellulose p-toluenesulfonyl carbamate have been found to exceed those reported for acidic cellulose derivatives (Table III-5). The value shown for the sulfonyl carbamate derivative represents an average of those evaluated.

The superior ion exchange capacities of the sulfonyl carbamate derivatives can be attributed to several factors. The primary one being that a high degree of substitution can be achieved under relatively mild conditions due to the enhanced reactivity of sulfonyl isocyanates. This allows a high degree of substitution to be attained without extensive degradation and a concomitant loss of physical properties. Another important factor in attaining a higher capacity is the high degree of substitution uniformity accomplished by forming a homogeneous solution of the product.

Ion exchange capacities of cellulose derivatives are limited by the degree of substitution of the ionogenic groups onto the cellulose substrate. This theoretical limitation can be calculated as follows:

Basis: 1 gram mole of cellulose

let A = ion exchange capacity in milliequivalents per gram  
and D.S. = degree of substitution

There is 1 equivalent for each sulfonyl carbamate unit

Thus the total equivalents per mole of cellulose = D. S.

The unit weight of cellulose is 162.0 and that of the attached pendant group is 197.0. Thus the number of milliequivalents per gram of cellulose can be calculated from Equation (III-9).

$$A = \frac{D. S.}{.162 + .197 D.S.} \quad (III-9)$$

TABLE III-5

A COMPARISON OF ION EXCHANGE CAPACITIES FOR  
CATIONIC ION EXCHANGE DERIVATIVES OF CELLULOSE

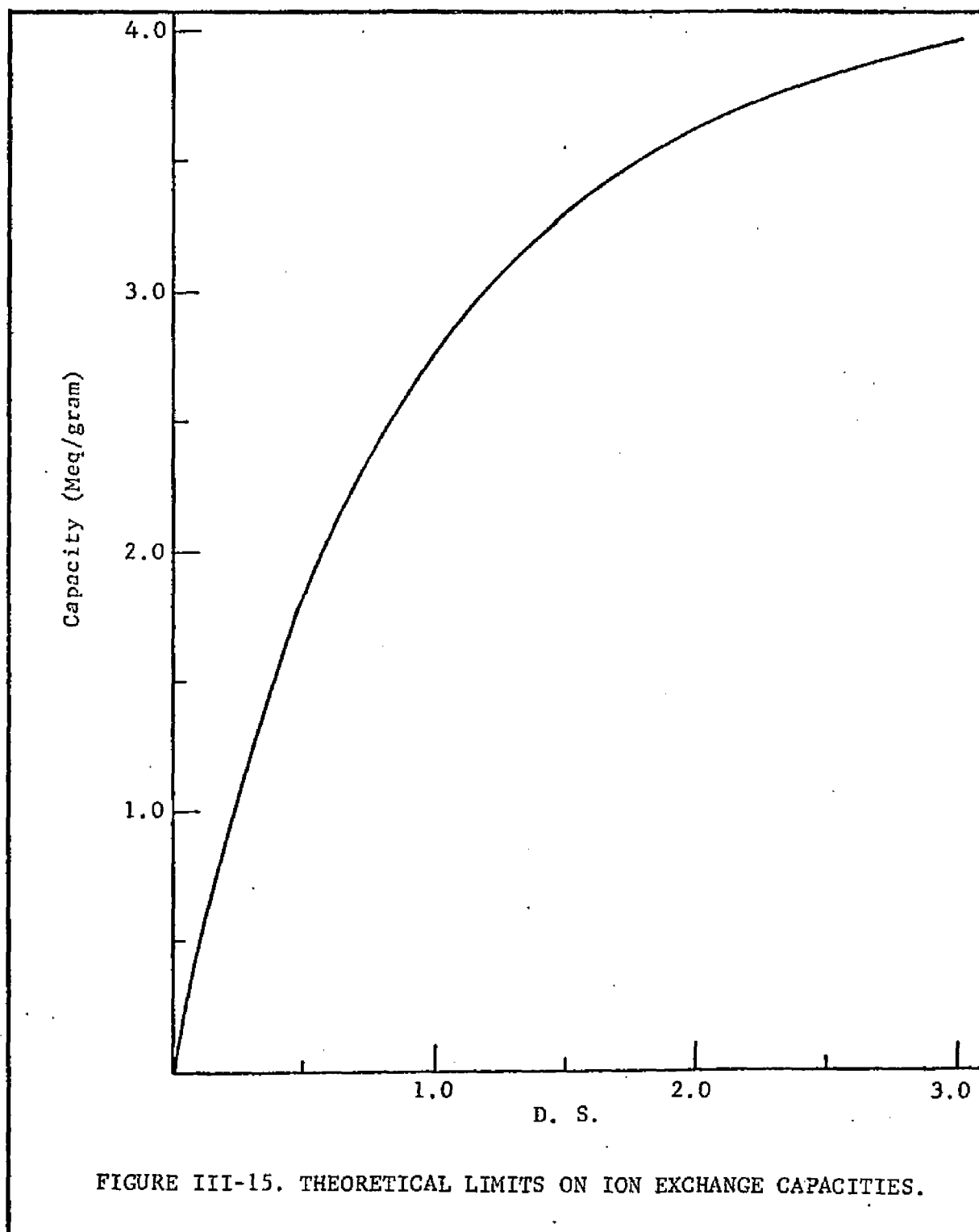
<u>Cellulose Derivative</u>	<u>Ionogenic Group</u>	<u>Acid Properties</u>	<u>Ion Exchange Capacity (Meq/g)</u>
	O		
p-toluenesulfonyl carbamate	-C-N-SO <sub>2</sub> -      -CH <sub>3</sub> H	weak acid	2.9
	O		
Carboxymethyl	-CH <sub>2</sub> -C-OH	weak acid	0.7 <sup>a</sup>
	O		
Partial succinate halfester	-CH <sub>2</sub> -C-OH	weak acid	1.0 <sup>a</sup>
Sulfoethylated	-CH <sub>2</sub> CH <sub>2</sub> -SO <sub>3</sub> H	strong acid	0.5 <sup>a</sup>
Phosphorylated	-PO <sub>3</sub> H <sub>2</sub>	strong acid	2.6 <sup>a</sup>

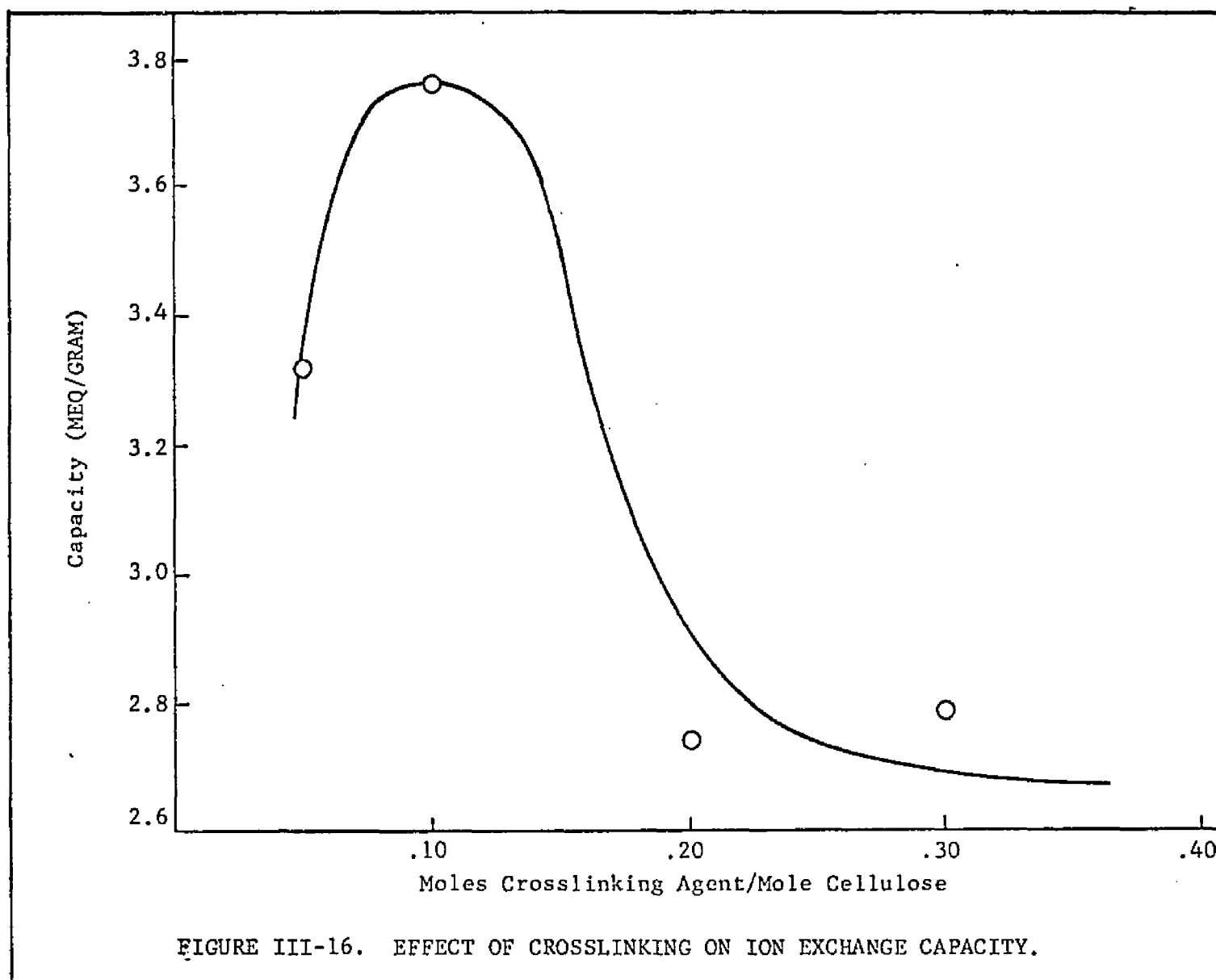
(a) reference III-5

From this equation the theoretical limit on the capacity can be determined for a given degree of substitution. Figure III-15 is a representation of this equation. A significant point brought out by this curve is the limiting return in ion exchange capacity for higher degrees of substitution. An increase in the D. S. from 2.0 to 3.0 requires approximately a fivefold increase in reaction time; yet this produces a theoretical increase in capacity of only about 0.4 meq./gram.

As discussed in Chapter I, ion exchange capacities are also affected by the extent of crosslinking present in the resin. The initial mole ratio of crosslinking reagent to cellulose was taken as a measure of the degree of crosslinking. Figure III-16 shows how crosslinking of cellulose *p*-toluenesulfonyl carbamate with methylene bis (*p*-phenyl isocyanate) effects its ion exchange capacity. These resins were of approximately identical degrees of substitution. The observed maximum is common to many other types of ion exchange resins as noted by Kunin (6) and is apparently due to the slight separation of the polymers molecules by the crosslinking agent, thus making the ionogenic groups more accessible. After more extensive crosslinking, these molecules are tightly bound at closer intervals making fewer ionogenic groups accessible for ion exchange and consequently lowering the capacity of the resin.

Ion exchange resins are of little use if they cannot be regenerated. Regeneration requires that the resin be flushed with a solution containing an excess of the ions originally attached to the ionogenic group. Experiments on the cellulosic sulfonyl carbamate resins show that regeneration of the acid form from the sodium salt can be





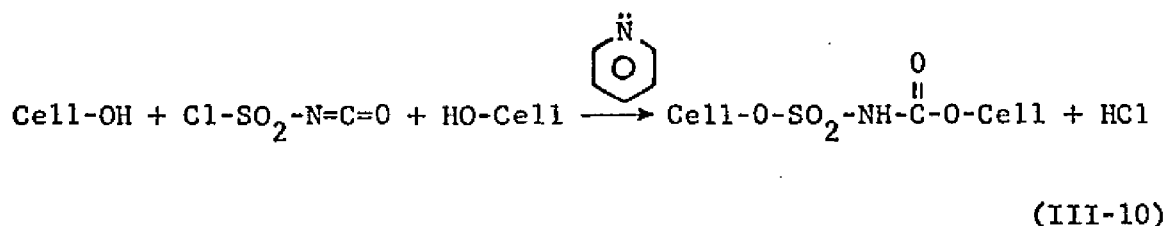
accomplished by washing the resins in aqueous solutions of HCl. For best results the pH of the system was kept in the 1.0-2.0 range. It has also been found that regeneration of the acid form is nearly quantitative and in fact the values for capacities shown in Figure III-16 were determined on resins that had been regenerated from the sodium salt by soaking in HCl at pH 1.0 for five days. Thus it can be seen that high capacities are possible even for the regenerated form.

If cellulose *p*-toluenesulfonyl carbamate is extensively cross-linked while in solution, the normal fibrous nature of the precipitated resin disappears. At low crosslinking ( $\sim 0.05$ ) the fibrous nature is maintained. When the fibrous structure is destroyed the purified polymer is recovered in a granular form, which is often more acceptable for fixed bed column operations.

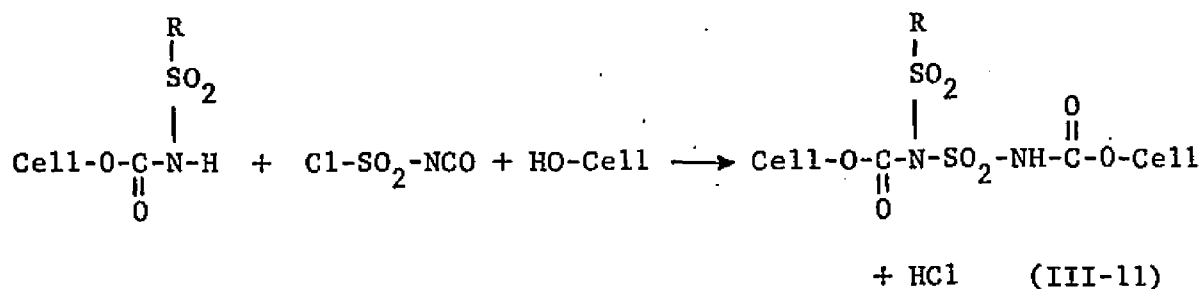
Ion exchange resins are usually designed to operate in fixed bed columns. Consequently, resins which swell on contact with the solutions being passed through the column are not acceptable. Swelling is minimized by crosslinking the polymer substrate to which the ionogenic groups are attached. The amount of crosslinking varies according to the system and thus general statements about the swelling of resins must be qualified by a description of the system in which swelling was observed. Since weakly acidic cation exchange resins are generally used in alkali systems the swelling of cellulose *p*-toluenesulfonyl carbamate was studied under alkaline conditions. It was found that degrees of crosslinking produced by 0.05 moles methylene bis (*p*-phenyl isocyanate) per mole of cellulose were satisfactory in limiting the swelling of the polymer in neutral to weakly basic systems while degrees of crosslinking of 0.15 were necessary for resins used at a

a pH of 10-12. As the degree of crosslinking increased from 0.05 to 0.20 a steady decrease in the amount of swelling could be observed in strongly alkaline solutions. Almost no swelling of the resin having a degree of crosslinking of 0.20 was noted. No significant reduction in capacity was observed at this crosslink density.

In addition to methylene bis (p-phenyl isocyanate) several other difunctional reagents were used to crosslink the sulfonyl carbamate derivatives. One of these, chlorosulfonyl isocyanate, produced a crosslink that was more stable than had been expected. It was postulated that chlorosulfonyl isocyanate would react with unsubstituted hydroxyl groups on the cellulose chain as shown in Equation (III-10). However



such a reaction forms a sulfonic ester bond to one of the cellulose chains and these types of structures are usually quite easily hydrolyzed by caustic. No such degradation was observed with the structure in this case, so that either this particular structure is more stable than regular sulfonic esters or the crosslinking mechanism may have followed a different path as shown in Equation (III-11) which suggests





the possibility of a reaction between the sulfonyl chloride and the acid hydrogen of the sulfonyl carbamate structure. This mechanism does not result in the formation of a sulfonic ester and should be more stable to hydrolysis.

Another successful reagent used for crosslinking was p-isocyanato phenylsulfonyl isocyanate, which formed a completely crosslinked matrix in approximately 15 minutes as compared to 3 to 4 hours for dissociates. Dichloro and trichloro acetic acid crosslinked the polymer but the products were not stable to alkaline hydrolysis. p-Sulfonyl chloride phenyl ether did not form a crosslinked system.

#### Film Applications

Films were cast from the solution formed in the reaction of p-toluenesulfonyl isocyanate with cellulose in pyridine. After the films were stripped from their glass backing they had good optical clarity. However as the films were dried the ones retaining transparency were found to have thicknesses of .0015 to .0019 inches. Those films with thicknesses of .0028 to .0032 inches became opaque on drying. All of the films were smooth and fiber free but retained a slight pale yellow color. There was some problem with bubbles forming in the film as it was cast. These could be circumvented by casting the film from a hot (60-70°C) solution. This decreased the solution viscosity so that any bubbles formed could rapidly escape without leaving pinholes in the films.

As the films dried they became very brittle. Di n-butyl phthalate was tried as a plasticizer by adding it to the polymer solutions before casting. Three plasticizer concentrations were used; 5, 10, and 15 percent of the initial weight of cellulose. As expected the flexibility

of the films was improved by the plasticizer. However, the only concentration giving excellent flexibility was 15 percent. Films of .0015 to .0017 inch thickness containing this amount of plasticizer could be flexed up to 50 times without fracture. The best results for the other plasticizer concentrations in films of the same thickness were 12 to 15 flexes for the 10 percent, 5 to 7 for the 5 percent and only 1 or 2 flexes for the unplasticized film. Even though 15 percent plasticizer gave the best results for flexibility, films containing this much plasticizer were opaque even in the .0015 inch thicknesses. Clarity was maintained in this film thickness with less than 10 percent plasticizer. All of the films exhibited low tensile strengths.

Other ways of removing pyridine from the films were also investigated. Coagulating the freshly cast film in ethanol gave a very brittle film of no transparency. X-ray diffraction of these films indicated that they contained twice the crystallinity of the air dried films (13% as compared to 6%). The same results were obtained when the film was washed in acetone or water.

Solubilities of the films were evaluated and are given in Table III-6. Because of the potential application of films in ion exchange, some way of insuring insolubility is required. Crosslinking of films using methylene bis (p-phenyl isocyanate) as well as chlorosulfonyl isocyanate was tried. The films were loosely wrapped around glass rods and immersed in the desired reaction system. Crosslinking with methylene bis (p-phenyl isocyanate) in benzene gave a film which was only slightly crosslinked as noted by the fact that it did not dissolve but did lose its shape and formed a gel in caustic and in dimethyl sulfoxide. This

TABLE III-6  
FILM SOLUBILITY

Solvent	Freshly Cast Film	Air Dried Film	Ethanol Coagulated Film
Acetone	S	S	I
Benzene	I	I	I
Water	I	I	I
2% NaOH	S	S	I
5% NaOH	I	I	I
10% NaOH	I	I	I
1N HNO <sub>3</sub>	I	I	I
Dimethyl sulfoxide	S	S	S
Dimethyl formamide	S	S	S

probably means that the large molecule being used to crosslink the polymer could not penetrate the film and crosslinking occurred only on the surface. Chlorosulfonyl isocyanate was applied to films in a benzene medium and neat. Both systems produced films insoluble in 2 percent sodium hydroxide and acetone, but they were soluble in dimethyl sulfoxide. Either the crosslinks were broken by dimethyl sulfoxide or the films became insoluble due to a physical process such as crystallization as the pyridine initially in the films was extracted.

#### Coating of Metals

Another application of cellulose *p*-toluenesulfonyl carbamate investigated was that of metals coating. It was found that the coatings formed by dipping the metal strips into the solution of polymer in pyridine produced a thicker, less uniform coat than when the polymer solution was applied to the strip with a small brush. Dip coating gave films almost twice as thick (~.0025 inches to .0015 inches) as brush application. There was considerable difficulty in removing pyridine from the coatings when applied in the thicker form. Often bubbling of the coating occurred when the thicker samples were dried and consequently there was no adhesion at these sites. Bubbling also gave a rough finish to the coating.

The metal strips were immersed in three general classes of solutions, caustics, acids, and organics. Benzene did not effect the coating and it appeared that there was little penetration to the metal being protected. The same was noted for chlorobenzene, a more polar solvent. When immersed in both .2N sodium hydroxide and 2N sodium hydroxide the coating was stripped off the metal in 2-3 hours. When

immersed in .2N sulfuric acid or 1N nitric acid the coatings were not effected, i.e. they remained clear and in tact, but the acid penetrated and corroded the metal. It is believed that the penetration was due to pinholes in the coating which occurred along the sharp edges at the bottom of the strips. Thus with the proper coating technique and better coating equipment this problem could be remedied and acid resistant coating obtained from this derivative.

The protection afforded metal strips in the general laboratory atmosphere were also observed. After two months of being exposed to these conditions, exposed metal was highly corroded and rusted while the coated metals were in perfect condition. Another interesting observation was that the metal strips which had been coated and then had the coating stripped off were well-protected and showed no rust or corrosion under the same conditions. This fact tends to indicate that a thin, possibly monomolecular, layer of the polymer has been bonded to the metal and simple stripping off of the layer of coating does not damage the protection of the metal. A photograph illustrating these results is given in Figure III-17. In this figure, strip A is polished and uncoated. Strip B has been coated, immersed in benzene for a week, and kept at laboratory atmosphere conditions for three months. The top portion of this strip was not coated and is completely rusted, while the coated portion is well protected. Strip C had the same treatment as B except the lower portion was peeled off and left at laboratory atmosphere conditions for 3 months. The top section had not been coated and is completely rusted. Both the section still having a coating as well as the section from which the coating had been stripped are unrusted and seem well-protected.

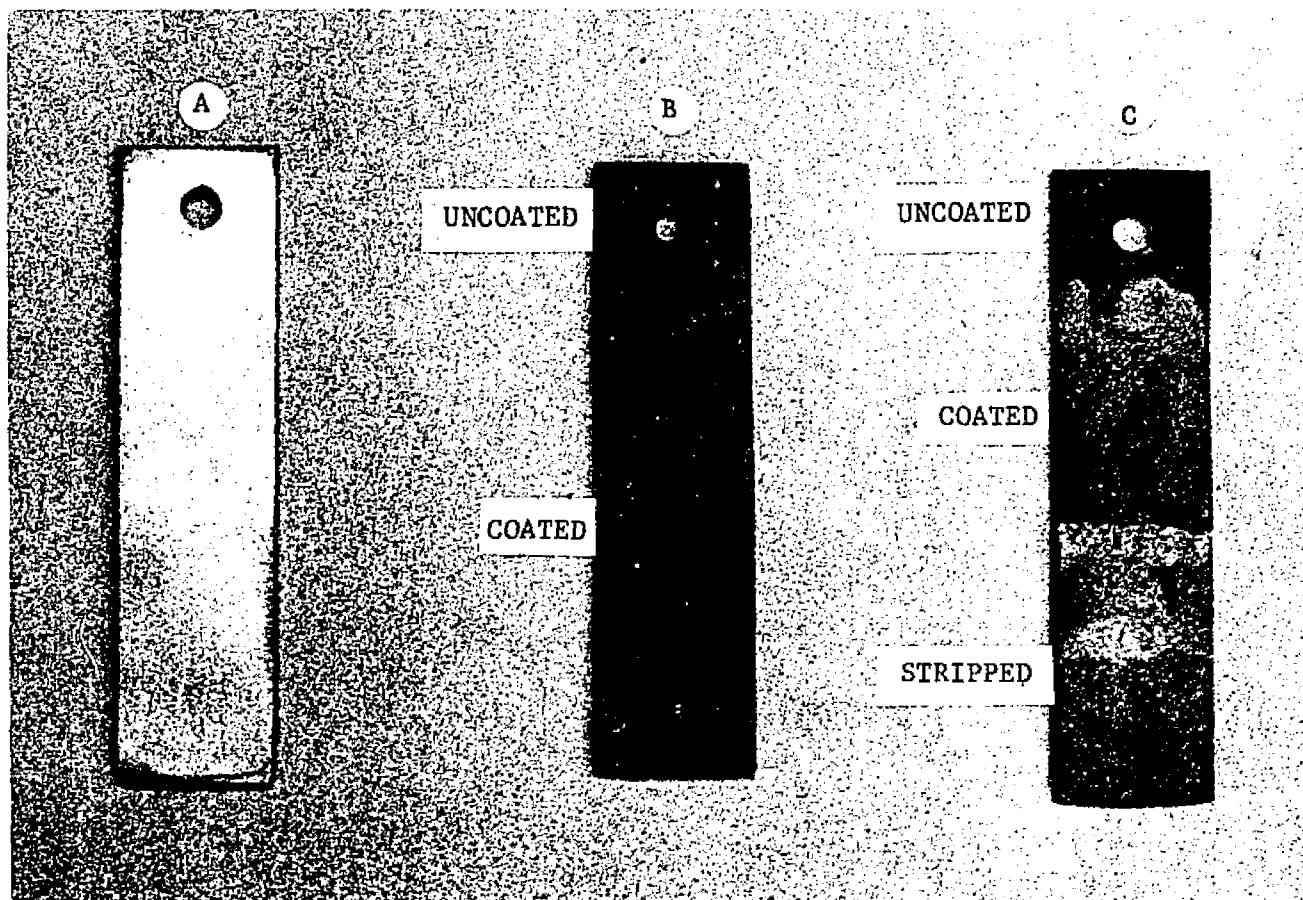
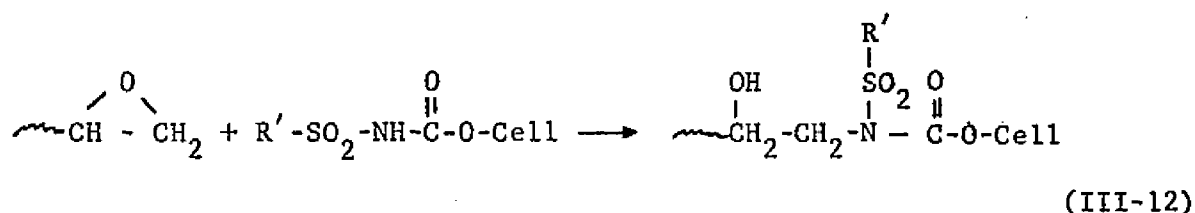


FIGURE III-17. PHOTOGRAPH OF CARBON STEEL STRIPS.

### Molding with Epoxy Prepolymers

Epoxy prepolymers are low molecular weight ( $\bar{M}_N \approx 1000$ ) polymers with epoxy ( $-\text{CH}-\text{CH}_2$ ) end groups. Before the studies on the thermal stability of sulfonyl carbamates showed them not to be as stable as they were thought to be, it was believed that a good material could be formed by reacting the epoxy end groups with the hydrogen of the carbamate linkage (Equation III-12). This should result in a highly cross-



linked polymeric system.

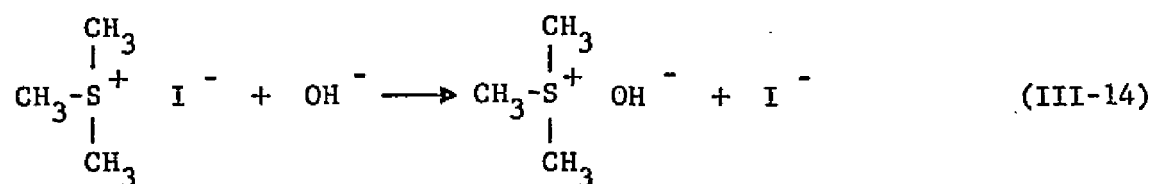
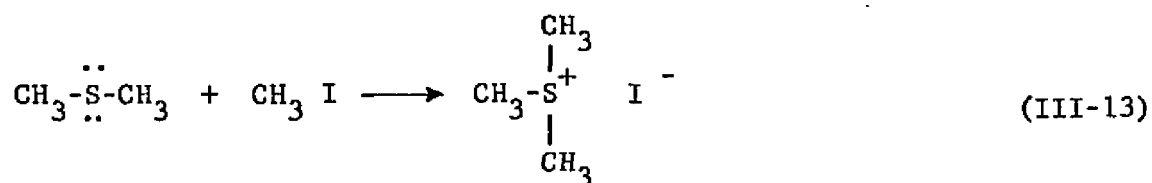
Reactions were run with both the dry purified cellulose derivative and with the pyridine solution of the cellulosic. It was found that when the epoxy was mixed with the pyridine solution the product formed turned black on standing and there was some difficulty in removing the pyridine. When a mixture of the dry polymer and the epoxy (5:4 weight ratio) was prepared and allowed to stand for 24 hours at room temperature a tough rubbery product was obtained. Heating the composite did not set it up into a more rigid form. Other ratios of polymer to epoxy were tried but at higher percentages of polymer, mixing was difficult and at higher percentages of epoxy the system did not set up.

### E. Other Work on Cellulose Derivatives

This section is devoted to those areas of research which were investigated but were not as fruitful as the work on sulfonyl isocyanates.

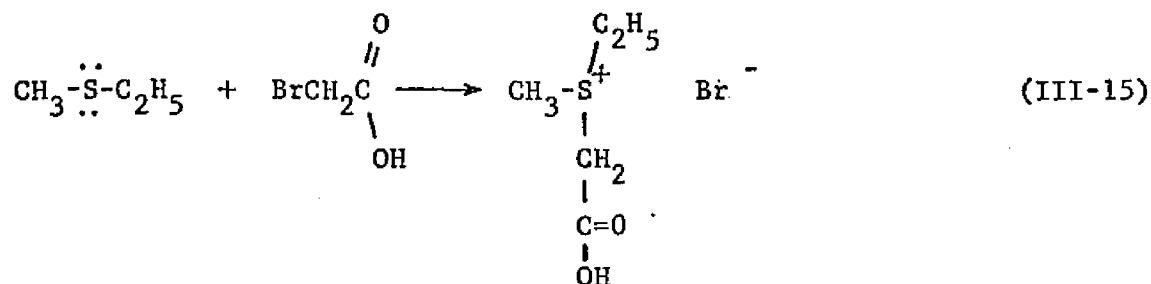
#### Reaction of Monochlorodimethyl Sulfide With Cellulose

Besides making a new cation exchange resin by forming sulfonyl carbamate derivatives of cellulose, some initially promising approaches to synthesizing anion exchange resins using a cellulose substrate were investigated. Perhaps the most interesting of these was the possibility of attaching a sulfide group to cellulose. The basic chemistry behind the ion exchange capabilities of such a derivative is essentially the same as that for tertiary amines and quaternary ammonium salts. The process of forming a sulfide salt is well known and is discussed by Roberts and Caserio (7) who report that dimethyl sulfide forms a salt with methyl iodide as shown in Equation (III-13). They further report that the hydroxide form as shown in Equation (III-14) forms strongly

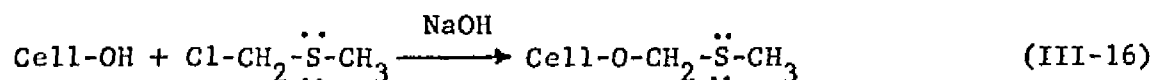


basic water solutions similar to a quaternary ammonium salt. A further possibility exists as shown in Equation (III-15). Here the final product would be useful as an amphoteric ion exchange resin.

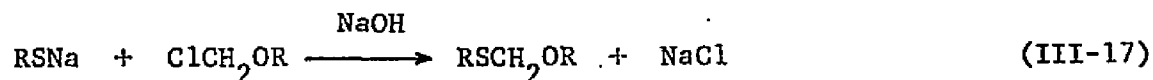




Commercial samples of monochlorodimethyl sulfide were obtained for the purpose of investigating the possibility of forming an anion exchange resin utilizing the theory of the previous paragraph. It was envisioned that the proposed derivative could be formed according to Equation (III-16).



Several problems were expected in getting this reaction to go as desired. Wenzel and Reid (8) claim that the thio acetal structure is stable except when acid is present. This would present a problem in using the cellulose derivative formed as an anion exchange resin, but it may still be useful if the trimerization step would provide an acid stable product. The same authors claim low yields for the reaction shown in Equation (III-17). This reaction is similar to that of



Equation (III-16) so that the same sort of yields might be expected.

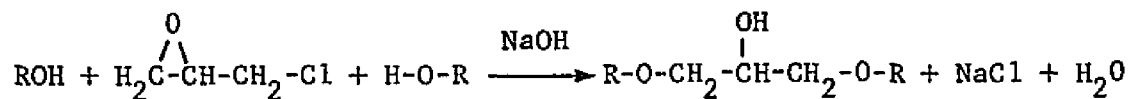
Low yields could also result from hydrolysis of the chloromethyl sulfide or from oxidation of the sulfide to a sulfoxide or a sulfone (9).

Even with these problems it was decided that it would be worthwhile to attempt the formation of the sulfide derivative. The reaction conditions used are shown in Appendix C. To date no successful runs have been made but further effort along these lines may be worthwhile.

#### Crosslinking of Carboxymethyl Cellulose

The application of carboxymethyl cellulose in ion exchange has been limited due to its low ion exchange capacity. It has a low capacity because the lack of good crosslinking procedures restricts the degree of substitution to a fairly low level. Ester forming and acetal forming functional groups have been used to crosslink CMC but these are unstable to basic and acid systems respectively. Carbamate linkages have not been practical in crosslinking CMC because of the anhydrous system required for such a process. It was therefore felt that the best crosslinking agent would be one which produced ether linkages (which are reasonably stable to both acid and basic environments).

Epichlorohydrin possesses two functional groups which react with hydroxyls to yield ether linkages (Equation III-18).



(III-18)

This theory has been tried on both commercial grade CMC and on that prepared in the laboratory. Data from these trials are given in Appendix C. To date a successfully crosslinked resin has not been

obtained but there are still some routes which have not been tried and which show some promise.

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## CHAPTER IV

### CONCLUSIONS AND RECOMMENDATIONS

#### A. Conclusions

1. The hydrogen atom in the sulfonyl carbamate structure is acid enough to act as a site for cation exchange reactions. This hydrogen has about the same acidity as acetic acid.
2. The sulfonyl carbamate linkage is sufficiently stable to alkaline solutions so that a cellulose derivative formed with this structure does not easily hydrolyze.
3. *p*-Toluenesulfonyl isocyanate reacts with untreated cellulose in the presence of pyridine to give cellulose *p*-toluenesulfonyl carbamate.
4. Temperature has a strong effect on the rate of reaction of *p*-toluenesulfonyl isocyanate with cellulose due to the poor solubility of a pyridine-*p*-toluenesulfonyl isocyanate complex formed on addition of the sulfonyl isocyanate to a pyridine-cellulose slurry.
5. The ion exchange capacity of the sulfonyl carbamate derivatives are much greater than those of previously reported cellulosic ion exchangers.
6. Swelling of the sulfonyl carbamate derivatives in alkaline solutions is controlled by the degree to which the polymer is crosslinked.
7. Ion exchange capacity of a resin goes through a maximum as its degree of crosslinking is increased.

8. Stable crosslinking is provided by methylene bis (p-phenyl isocyanate), chlorosulfonyl isocyanate, and p-isocyanato phenylsulfonyl isocyanate.
9. The physical nature of the resin is changed by the degree of crosslinking; becoming more granular as the crosslinking is increased.
10. Another application of sulfonyl carbamate derivatives of cellulose which looks promising is as a film. Clear films may be cast from the pyridine reaction solution.
11. The reactivity of sulfonyl isocyanates provides a route to a series of mixed cellulose derivatives without need for special pretreatment of the cellulose or the application of swelling agents.
12. The thermal stability of sulfonyl carbamates is not as high as had been predicted from studies on aryl isocyanates. This is due to a change in decomposition mechanism caused by the addition of the sulfone group into the carbamate structure.
13. Metals coating using sulfonyl carbamate derivatives of cellulose would provide protection from acid and/or organic environments but not from alkali systems.
14. The active hydrogen of the sulfonyl carbamate structure provides a site for the ring opening type of reaction necessary to set up an epoxy prepolymer into a three dimensional block copolymer.
15. Chloroalkyl sulfides do not react with alkali cellulose under mild conditions to produce the thio acetal structure expected from a Williamson type reaction.

## B. Recommendations

1. The possibility of using sulfonyl carbamates as ion exchangers has been proven by this work. Their application, and those of most ion exchange celluloses, will probably be limited to specialty type applications. Therefore, I recommend that research be carried out showing the utility of these resins in fractionation and separation of proteins, nucleic acids, and other biological chemicals.
2. I also recommend that research be conducted as to the existence of systems, not biologically oriented, which may have separation problems solvable by sulfonyl carbamate structures.
3. The investigation of other sulfonyl isocyanates as reactants for the formation of sulfonyl carbamate derivatives may be profitable. The properties of such derivatives may be vastly different and in fact superior to the p-toluene derivative.
4. Amphoteric ion exchange resins have many useful applications. Such resins could be synthesized by reacting p-dimethyl amino benzene-sulfonyl isocyanate with cellulose. The synthesis as well as evaluation of such materials would be profitable.
5. The work on films should be extended. Particularly important is the area of purification; a system for rapidly drying the film and quantitative removal of the solvent should be developed. Also of interest would be the application of sulfonyl carbamate films in specialty areas such as ion exchange and biological studies.
6. No work has been found in the literature on reacting sulfonyl isocyanates with other substrates such as polyvinyl alcohol. The

properties of such materials may indeed be worth investigating.

7. Mixed derivatives have only been superficially examined in this research. One cannot ignore the possibilities that may exist as regards these materials. An almost infinite number of combinations exist and only few have been investigated. A massive effort involving study on both synthesis and properties would be required to cover so broad an area.
8. An area attracting much attention from a variety of professions is that of artificial organs. The major problem with such an endeavor is finding a material of construction which does not cause thrombosis. It has been postulated that the incorporation of charged sites into such materials may contribute to their utility. I believe that sulfonyl carbamates should be evaluated for such an application not only as attached to a cellulose substrate but also as substituents on other polymers or copolymers.



## APPENDIX A

TYPICAL EXPERIMENTAL DATA ON THE REACTION OF  
p-TOLUENE SULFONYL ISOCYANATE WITH CELLULOSE

APPENDIX TABLE A-1

## DATA ON THE EFFECT OF REACTION TEMPERATURE

Experiment No.	Substrate	Reactant	Medium	Reactant to Substrate Ratio	Reaction Temperature	Reaction Time	D. S.
14-69-1	cotton linters	pTSI*	pyridine	4:1	60°C	1 hr.	0.56
14-69-2	cotton linters	pTSI	pyridine	4:1	60°C	1 hr.	0.41
14-69-3	cotton linters	pTSI	pyridine	4:1	70°C	1 hr.	0.39
14-69-4	cotton linters	pTSI	pyridine	4:1	70°C	1 hr.	0.42
14-69-5	cotton linters	pTSI	pyridine	4:1	85°C	1 hr.	2.25
14-69-6	cotton linters	pTSI	pyridine	4:1	85°C	1 hr.	2.12
14-69-7	cotton linters	pTSI	pyridine	4:1	95°C	1 hr.	--
14-69-8	cotton linters	pTSI	pyridine	4:1	95°C	1 hr.	2.40

\*p-toluenesulfonyl isocyanate

# APPENDIX TABLE A-2

## DATA ON REACTION RATE

Experiment No.	Substrate	Reactant	Medium	Reactant to Substrate Ratio	Reaction Temperature	Reaction Time	D. S.
14-74-1	cotton linters	pTSI*	pyridine	4:1	70°C	1 hr.	0.52
14-74-2	cotton linters	pTSI	pyridine	4:1	70°C	2 hr.	0.84
14-74-3	cotton linters	pTSI	pyridine	4:1	70°C	3 hr.	1.35
14-74-4	cotton linters	pTSI	pyridine	4:1	70°C	4 hr.	1.62
14-74-5	cotton linters	pTSI	pyridine	4:1	70°C	5 hr.	1.99
14-74-6	cotton linters	pTSI	pyridine	4:1	70°C	6 hr.	2.28
14-74-7	cotton linters	pTSI	pyridine	4:1	70°C	9.5 hr.	2.42
14-74-8	cotton linters	pTSI	pyridine	4:1	70°C	48 hr.	3.06

\*p-toluenesulfonyl isocyanate

APPENDIX TABLE A-3

## DATA ON INITIAL REACTANT RATIO

Experiment No.	Substrate	Reactant	Medium	Reactant to Substrate Ratio	Reaction Temperature	D. S.
16-14-1	cotton linters	pTSI <sup>*</sup>	pyridine	0.5:1	80°C	~ 0
14-96-1	cotton linters	pTSI	pyridine	1:1	80°C	.05
14-96-2	cotton linters	pTSI	pyridine	2:1	80°C	.55
14-96-3	cotton linters	pTSI	pyridine	3:1	80°C	2.25
14-96-4	cotton linters	pTSI	pyridine	4:1	80°C	~ 3
14-96-5	cotton linters	pTSI	pyridine	5:1	80°C	2.25
14-96-6	cotton linters	pTSI	pyridine	6:1	80°C	~ 3
14-96-7	cotton linters	pTSI	pyridine	7:1	80°C	--

\*p-toluenesulfonyl isocyanate

APPENDIX TABLE A-4

DATA ON TESTING OF REACTION MEDIA FOR  
REACTION OF CELLULOSE AND pTSI\*

Experiment No.	Medium	Reactant to Substrate Ratio	Reaction Temperature	Reaction Time	Results
14-36-1	chlorobenzene	3:1	80°C	6 hrs.	no reaction
14-37-1	p-xylene	3:1	75°C	8 hrs.	no reaction
14-38-1	pyridine with ZnCl <sub>2</sub> :pyridine	3:1	65°C	14 hrs.	0.86 D.S.
14-39-1	pyridine with ZnCl <sub>2</sub> :pyridine	4:1	80°C	18 hrs.	1.58 D.S.
14-49-1	neat	4:1	25°C	18 hrs.	no reaction
14-107-1	benzene	4:1	80°C	18 hrs.	no reaction
14-107-1	chlorobenzene	4:1	80°C	18 hrs.	no reaction
14-112-1	dioxane	4:1	80°C	18 hrs.	no reaction
16-1-1A	neat	10:1	90°C	18 hrs.	no reaction
16-1-1B	neat	30:1	90°C	18 hrs.	no reaction

\*p-toluenesulfonyl isocyanate

APPENDIX TABLE A-4 (Continued)

Experiment No.	Medium	Reactant to Substrate Ratio	Reaction Temperature	Reaction Time	Results
16-40-1A	60% benzene 40% pyridine	5:1	80°C	18 hrs.	no reaction
16-40-1B	triethylamine	5:1	80°C	18 hrs.	no reaction
16-45-1	triethylamine 95% pyridine	5:1	80°C	18 hrs.	degradation of polymer

APPENDIX TABLE A-5

DATA ON EFFECT OF INITIAL AMOUNT OF PYRIDINE  
PRESENT ON REACTION OF PTSI\* WITH CELLULOSE

Experiment No.	Mole Ratio pTSI:Cellulose	Reaction Temperature	Reaction Time	ml of pyridine per gram of cellulose	Weight Gain
16-12-1	4:1	85°C	18 hrs.	2	60%
16-12-2	4:1	85°C	18 hrs.	4	100%
16-12-3	4:1	85°C	18 hrs.	10	80%
16-12-4	4:1	85°C	18 hrs.	20	130%
16-12-5	4:1	85°C	18 hrs.	30	100%
16-12-6	4:1	85°C	18 hrs.	50	140%
16-12-7	4:1	85°C	18 hrs.	60	140%

\*p-toluenesulfonyl isocyanate

## APPENDIX B

### TYPICAL DATA ON ION EXCHANGE EVALUATION OF SULFONYL CARBAMATES



## APPENDIX TABLE B-1

## DATA ON TITRATION OF SULFONYL CARBAMATES

sample weight = 1.6172 grams

Milliliters of Base Added	Normality of Base	Total Meq. of Base Added	Total Meq. of Base Per Gram of Sample	pH
0		0	0	4.3
1.0	0.2043	0.2043	0.1263	4.6
1.0	0.2043	0.4086	0.2526	4.8
1.0	0.2043	0.6129	0.3789	4.96
1.0	0.2043	0.8172	0.5052	5.10
1.0	2.0097	2.8269	1.7480	5.80
1.0	2.0097	4.8366	2.9907	
1.0	0.2043	5.0409	3.1170	7.55
1.0	0.2043	5.2452	3.2433	9.30
2.0	0.2043	5.6538	3.4959	10.50
2.0	0.2043	6.0624	3.7485	11.23
2.0	0.2043	6.4710	4.0011	11.55
2.0	0.2043	6.8796	4.2537	11.75
2.0	0.2043	7.2882	4.5063	12.00
2.0	0.2043	7.6968	4.7589	12.10
2.0	0.2043	8.1054	5.0115	12.11

# APPENDIX TABLE B-2

## DATA ON EFFECT OF DEGREE OF CROSSLINKING ON ION EXCHANGE CAPACITY

Substrate	Crosslinking Agent	Moles of Crosslinking Agent Per Mole of Initial Cellulose	Ion Exchange Capacity (Meq./Gram)
CPTSC <sup>*</sup>	MBPI <sup>**</sup>	0.05:1	3.34
CPTSC	MBPI	0.10:1	3.75
CPTSC	MBPI	0.15:1	2.90
CPTSC	MBPI	0.20:1	2.74
CPTSC	MBPI	0.30:1	2.80

\* cellulose p-toluenesulfonyl carbamate

\*\* methylene bis-(p-phenyl isocyanate)

## APPENDIX C

### TYPICAL WORK ON NON-CARBAMATE CELLULOSE DERIVATIVES

APPENDIX TABLE C-1

REACTION OF MONOCHLORODIMETHYL SULFIDE  
WITH CELLULOSE

Experiment No.	Solvent	Catalyst	MCDMS <sup>*</sup> : Cellulose	Temperature	Time	Reactor
14-114-1	i-PrOH	NaOH	3:1	60°C	3.75 hrs.	I
14-117-1	i-PrOH	NaOH	3:1	80°C	3 hrs.	I
14-118-1	neat	NaOH	3:1	25°C 50°C 70°C	2.5 hrs. 1 hr. 2.5 hrs	II
16-7-1	pyridine	none	5:1	65°C	8 hrs.	III
16-7-2	pyridine	NaOH	5:1	65°C	8 hrs.	III
16-7-3	t-BuOH	NaOH	5:1	65°C	8 hrs.	III
16-7-4	DMSO	NaOH	5:1	65°C	8 hrs.	III
16-15-1	PrOH	NaOH	6:1	25°C	16 hrs.	I

NOTE: All recovered solids were washed in isopropyl alcohol and isopropyl alcohol-water mixtures before being dried in a vacuum oven.

I - 1 liter round bottom flask

II - 4 liter scraped surface reactor

III - 50 ml sealed reactor

APPENDIX TABLE C-2

## CROSSLINKING OF CARBOXYMETHYL CELLULOSE

Experiment No.	Solvent	Catalyst	Crosslinking Agent	Temperature	Time	Reactor
14-1-1	i-PrOH	NaOH	epichlorohydrin	25°C	1.5 hrs.	I
				70°C	1.75 hrs.	
14-2-1	i-PrOH	NaOH	epichlorohydrin	85°C	2.5 hrs.	I
14-3-1	Xylene	NaOH	epichlorohydrin	105°C	3 hours	II
14-4-1	Xylene	NaOH	epichlorohydrin	125°C	3 hours	II
14-26-2	i-PrOH	NaOH	dichloroacetic acid	40°C	36 hours	II
14-26-2A	none	NaOH	dichloroacetic acid	80°C	8 hours	III
16-30-1	none	NaOH	epichlorohydrin	80°C	2 hours	IV

Note: Product from 14-26-2A was water insoluble

- I - heavy walled glass reactor
- II - round bottom flask
- III - vacuum oven
- IV - scraped surface reactor

VITA

Ronald William Rousseau was born in Bogalusa, Louisiana on September 28, 1943. His family moved to Baton Rouge, Louisiana in 1945 where he has since resided. He has three sisters and a brother, all younger than he. After graduation from Redemptorist High School in May 1961, he entered Louisiana State University obtaining a B. S. degree in Chemical Engineering in January, 1966 and a M. S. degree in Chemical Engineering in January, 1968.

In 1963 he married Tess Marie McKinney and they now have three sons Ronald William, David Patrick, and Brett Charles.

In the summers of 1964 and 1966 he was employed by Ethyl Corporation as a Development Engineer and in the summers of 1967 and 1968 as an Instructor in the Department of Chemical Engineering at L.S.U. He has accepted a position as Assistant Professor of Chemical Engineering at North Carolina State University in Raleigh, North Carolina beginning September, 1969. He will spend the forthcoming summer employed by West Virginia Pulp and Paper Company in Charleston, South Carolina.

# EXAMINATION AND THESIS REPORT

Candidate: Ronald William Rousseau

Major Field: Chemical Engineering

Title of Thesis: Ion Exchange Derivatives of Cellulose

Approved:

Clayton D. Collier  
Major Professor and Chairman  
R. D. Anderson  
Dean of the Graduate School

EXAMINING COMMITTEE:

Ralph W. Pike  
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Date of Examination:

May 13, 1969